

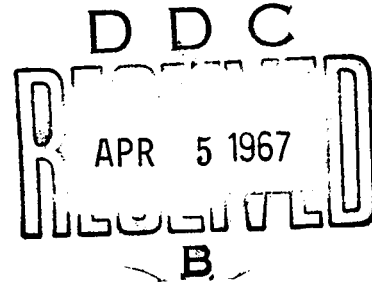
TASK I REPORT

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DEVELOPMENT OF DISPERSION-STRENGTHENED,
NICKEL-MOLYBDENUM,
NONOXIDATION-RESISTANT ALLOYS

by

R. C. Nelson
R. Widmer



Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Contract NAS 3-7265

Technical Management, Lewis Research Center
Spacecraft Technology Division
Cleveland, Ohio

F. H. Harf, Project Manager
L. F. Norris, Research Advisor

June 1966

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DEVELOPMENT OF DISPERSION-STRENGTHENED, NICKEL-MOLYBDENUM NONOXIDATION-RESISTANT ALLOYS

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ABSTRACT

The development of a nickel/molybdenum-base alloy having a 3000-hour stress rupture strength of 15,000 psi at 2000° F was undertaken. It is expected that a fine dispersion of thorium oxide and aluminum oxide will increase the strength of the matrix alloy to this level. Processing parameters for the preparation of such an alloy were investigated. Seven alloys including one which contained no dispersoid were prepared by selective reduction of oxides. The matrix was nickel-15% molybdenum, and 2, 5 and 7.5 % alumina or thoria was added. Fine nickel and molybdenum oxides were used as precursors for the matrix metal; the dispersed phase was introduced by mechanical mixing for alumina and by thermal decomposition of nitrates for thoria.

These alloys were extruded and their structures were evaluated by optical and electron microscopy techniques before and after stability tests at 2000° F in vacuum.

Recommendations for high temperature stress rupture testing of three selected alloys were made.

FOREWORD

This report covers the work performed under NASA Contract NAS 3-7265 during the period from 24 March 1965 to 30 April 1966.

This contract was initiated between NASA Lewis Research Center and the New England Materials Laboratory, Inc. for the "Development of Dispersion-Strengthened, Nickel-Molybdenum, Nonoxidation-Resistant Alloys." Technical direction was supplied by Mr. F. H. Harf, Project Manager of the Lewis Research Center, Spacecraft Technology Division, Cleveland, Ohio. Dr. L. F. Norris of the Materials and Structures Division was the NASA Research Advisor.

Mr. Richard C. Nelson of the New England Materials Laboratory was the Project Engineer in charge. Dr. Robert Widmer was the Program Manager. Technical assistance was provided by Dr. Allan S. Bufferd. Dr. Nicholas J. Grant of M.I.T. was an advisor to the program. Messrs. Allan R. Runge and David Kushinsky; Mrs. Edwin Johnson and Miss Ursula Jahnigen assisted in the execution of the experimental work.

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DEVELOPMENT OF DISPERSION-STRENGTHENED, NICKEL-MOLYBDENUM, NONOXIDATION-RESISTANT ALLOYS

by R. C. Nelson and R. Widmer

New England Materials Laboratory, Inc.

S U M M A R Y

Studies of the nickel/molybdenum-thorium oxide or aluminum oxide systems to develop nonoxidation-resistant, dispersion-strengthened alloys were undertaken. The matrix was nickel-15% molybdenum to which was added 2, 5 and 7.5 ^v/o alumina or thoria. Processing parameters studied included the following:

1. Preparation of matrix oxide powders by attrition grinding.
2. Methods of introducing the aluminum oxide and the thorium oxide. (The average particle size of these should be 0.02 (or less) to 0.1 microns; the average interparticle spacing should be 0.3 (or less) to 1.0 microns.)
3. Conditions for the selective reduction of the matrix oxides.
4. Consolidation of powders.
5. Extrusion variables.
6. Evaluation of the extruded structures by
 - (a) Density.
 - (b) Thermal stability at 2000° F.
 - (c) Chemical analysis for impurities.
 - (d) Lineal analysis.
 - (e) Microstructural examination by optical and electron microscopy.

On the basis of the structural analysis before and after the thermal stability tests, three alloys were recommended for the evaluation of mechanical properties to be carried out in Task II. The selected materials are those containing 2 ^v/o thoria, 5 ^v/o thoria, and 2 ^v/o alumina, respectively.

I. INTRODUCTION

Most of the currently available superalloys are primarily dependent on a matrix strengthened by a finely dispersed intermetallic compound such as $\text{Ni}_3(\text{Al}, \text{Ti})$ which is precipitated by an aging reaction. The resolution of this type of a dispersoid at temperatures higher than 900°C (1652°F) can lead to an overaged structure and a rapid drop of the high temperature strength properties with long time applications. Therefore, the obvious way to extend the useful temperature range of superalloys is to dispersion strengthen the matrix with a second phase stable at higher temperature. A fine particle size and a good dispersion also are necessary.

The stability of a second-phase particle is promoted by various factors, such as (1) low solubility of the second-phase constituents in the matrix, (2) large negative free energy of formation, (3) high melting temperature, (4) no reaction of second phase with other constituents. The most important stability factor from a thermodynamic point of view is the free energy of formation at high temperature. Since oxides tend to have a higher free energy of formation than carbides or most intermetallic compounds, one is led to the choice of oxides as the second phase. In particular on the basis of the free energy of formation criterion and previous experimental work in this field, thorium oxide and aluminum oxide become the preferred choices.

Several powder metallurgy techniques have been investigated in preparing dispersion-strengthened nickel (1, 2, 3, 4). Each of these methods has produced dispersion-strengthened material with high temperature properties significantly improved over those of the base metal without dispersoid.

The desire to apply the same principle to solid solution alloy matrices is an obvious one, as one aims to attain increased high temperature strength. Prior investigations on the strength properties of binary nickel alloys (5) indicate that molybdenum is one of the most effective solid solution strengtheners in nickel with additions in excess of 15 weight percent.

In applying to alloy matrices the techniques used in the dispersion strengthening of pure metals a limitation is imposed, as alloy powders are not commercially available with a particle size of 1 micron or less. On the other hand, oxides of various potential matrix metals are available or can easily be produced in desired purity and particle size.

In utilizing fine oxide powders for producing alloy matrices strengthened by dispersoids a very attractive technique was developed by

Rasmussen and Grant ⁽⁶⁾. In this method, fine nickel oxide and molybdenum oxide particles are coated with thorium oxide by a salt decomposition technique. The mixture is then subjected to a hydrogen atmosphere at elevated temperatures which preferentially reduces nickel oxide and molybdenum oxide. Following this selective reduction, the powder mixture (consisting of nickel and molybdenum coated with thorium oxide) is compacted and extruded.

Of particular concern is the extent of alloying between the nickel and molybdenum during the high temperature consolidation. Rasmussen's work ⁽⁶⁾ indicated that homogenization was indeed accomplished during the extrusion operation, due to the combination of high pressure and high temperature applied to a very fine particle size powder. At the same time, it appeared that the oxide dispersion was not changed significantly.

It was thus the objective of this program to develop a nonoxidation-resistant, nickel-base alloy for turbine buckets. A composition of nickel with 15% molybdenum and thorium oxide or aluminum oxide was made using essentially the Rasmussen/Grant selective reduction process.

II. PRELIMINARY PROCESSING EXPERIMENTS

Although the process to be used for the preparation of dispersion-strengthened, nickel-molybdenum alloys was known in principle, a number of preliminary experiments were necessary to determine specific details:

1. Nickel oxide was available with a particle size of 0.6 micron, but a particle size of 0.1-0.2 micron was desired. Further comminution of the powder was necessary by a suitable technique which would not cause contamination. Molybdenum dioxide was purchased as an 8-micron powder. Comminution parameters for this oxide had to be established.
2. The optimum condition for the introduction of thorium oxide had to be determined.
3. Experiments had to be conducted on the selective reduction of the oxides.
4. The method of consolidation prior to extrusion had to be studied.

The materials listed in Table I were procured for use in the processing experiments and in the preparation of the alloys. The emission spectrographic analyses of the two matrix oxides are shown in Table II.

1. Preparation of Fine Nickel Oxide and Molybdenum Dioxide Powders

Nickel oxide and molybdenum dioxide with an average particle size of approximately 0.1 to 0.2 microns were prepared by attrition grinding. The attritor unit, shown in Figures 1 and 2, is composed of a stationary, water-cooled tank and a rotating, spiked shaft, which moves the ball, powder and liquid charge.

Initial grinding experiments were conducted in a stainless steel unit with stainless steel balls; isopropyl alcohol was the grinding fluid. Comminution of other materials had been successfully performed under these conditions with a 0.5-micron powder being prepared usually after two days of grinding. The particle size evaluation of the ground powders was by Fisher Sub-sieve analysis and by electron microscopy techniques. After 40 and 63 hours of grinding, respectively, the nickel oxide and molybdenum dioxide were comminuted to 0.1 to 0.2 microns. During the early grinding studies, discrepancies were noted between the methods of measuring particle size. Caking of the powders after evaporation of the grinding fluid prevented an accurate evaluation by the sub-sieve analyzer method. All subsequent measurements were made by the electron microscopy method.

Chemical analyses of the ground powders, shown in Table III, indicated wear of the attritor components. Further grinding was then conducted in a porcelain attritor with porcelain balls. Contamination was so gross that further grinding with this system was discontinued. Subsequent grinding was conducted with modifications of the attritor components. A hard-facing nickel compound (92% nickel-8% phosphorus) was plated on the stainless steel unit. This plating was then replaced with a pure nickel one after it was decided that any phosphorus contamination should be avoided.

The final modification included the fabrication of a tank and shaft of pure nickel and the use of nickel shot as the grinding balls. Abrasion introduced a certain amount of nickel which required that its presence be taken into account in making up the composition of alloys.

2. Introduction of Thorium Oxide by Decomposition of Thorium Nitrate

Past experience had shown that the decomposition of thorium nitrate onto metal (or oxide) powders provides a method of producing fine thorium oxide in intimate contact with the base material.

General considerations as well as prior experimental work (1, 6) indicate that a low decomposition temperature is desirable, as it can be expected that the particle size is smaller the lower the temperature. In Table IV thoria crystal sizes are listed (as determined by x-ray diffraction) with varying decomposition temperatures. The data show (a) that thorium oxide is indeed formed at a temperature as low as 480° C, and (b) that larger thoria crystals are present after decomposition at temperatures above 800° C.

Changing the atmosphere did not seem to have much of an effect; it was decided that hydrogen would very definitely be undesirable because it would cause partial reduction of the matrix oxides. For this reason argon was considered the most suitable atmosphere.

3. Selective Reduction of Oxides

The reduction of nickel oxide by hydrogen proceeds significantly at temperatures above 427° C (800° F), but appreciable reduction of molybdenum dioxide occurs only above 815° C (1500° F). In preparing alloys containing a dispersoid such as thorium oxide or aluminum oxide in a matrix of nickel and molybdenum oxides careful examination is necessary after reduction of the matrix oxides to establish the following:

- (a) Was there any growth of thorium oxide or aluminum oxide under the conditions required to reduce the matrix oxides?
- (b) What is the residual oxygen content of the system after reduction?
- (c) Was there any sintering of the powders during the reduction?

Various reduction experiments were conducted to establish the most suitable conditions for the reduction of the nickel

oxide and molybdenum dioxide mixtures in the presence of a stable second phase.

Initial studies were conducted in a vertical fluidized bed, but this turned out to be too much of an undertaking within the scope of this program. (For further details see Appendix 1.)

Reduction studies were subsequently conducted in a horizontal tube furnace which had a diameter of 2 3/4 inches and a hot zone of approximately 8 inches. Nickel boats (made of 20% dense felt metal) contained the 100-gram charge per tube. A flow rate of 4 CFH of hydrogen was used.

The reduced powder was evaluated to determine oxygen content (by vacuum fusion analyses). Crystal size of thorium oxide or aluminum oxide (by x-ray diffraction) and shape and size of the thorium oxide or aluminum oxide (by electron microscopy using oxides extracted electrolytically from the matrix) were determined. The data are recorded in Tables V and VI and representative electron micrographs of thoria particles are presented in Figure 3.

In considering the temperature range of reduction, one finds that more efficient reduction takes place with increasing temperature without appreciable thoria crystal growth up to 1200° C. Five hours at 1100° C appear to give about the same results as one hour at 1200° C. The results obtained with x-ray diffraction are generally borne out by the electron microscopic examination. Extracted thoria particles were used to determine particle size.

It should be pointed out, however, that all these data are only of limited value because of inherent inadequacies of these techniques. Reliable information on particle size can only be obtained on the basis of electron microscopy on consolidated material.

Oxygen analysis by vacuum fusion is also of limited value; the data can only be used for comparison purposes.

In reducing the matrix oxides of those alloys containing alumina, no growth of the alumina crystal sizes was noticed when the powders were subjected to the same processing conditions as the thoria-containing alloys. The data obtained in these studies are recorded in Table VI.

4. Consolidation

Four methods of consolidation of powders prior to extrusion were considered:

- (a) cold compaction,
- (b) cold compaction followed by sintering,
- (c) hot compaction,
- (d) no precompaction (direct powder extrusion).

A small cold compact was prepared with one alloy powder which turned out to be successful. The slug had a density of 65% of theoretically 100% dense material. For various reasons methods b, c and d were discarded: It was thought that high temperature sintering of the uncanned compact should be avoided because of possible contamination. Hot compaction, although desirable, turned out to be very expensive. Direct powder extrusion has proven to be successful in the past; however, it would have been difficult to get the desired reduction ratio in extrusion.

III. PREPARATION OF ALLOYS

1. Alloy Compositions

In selecting the composition of the matrix, a nickel alloy with molybdenum content of 15% was chosen, which according to the literature ⁽⁵⁾ displays highest solid solution strengthening without second phase formation. The three volume fractions of each dispersed phase provide adequate variation in the loading of the matrix and yet avoid brittle structures.

The alloys prepared and evaluated were the following:

- #1 Nickel-15% molybdenum
- #2 Nickel-15% Molybdenum - 2.0 ^v/o Thorium Oxide
- #3 Nickel-15% Molybdenum - 2.0 ^v/o Aluminum Oxide
- #4 Nickel-15% Molybdenum - 5.0 ^v/o Thorium Oxide
- #5 Nickel-15% Molybdenum - 5.0 ^v/o Aluminum Oxide
- #6 Nickel-15% Molybdenum - 7.5 ^v/o Thorium Oxide
- #7 Nickel-15% Molybdenum - 7.5 ^v/o Aluminum Oxide

2. Description of Alloy Processing

The exact method of alloy preparation was chosen partially on the basis of prior work (1, 6), partially on the basis of preliminary experiments described in the previous section. The various steps are summarized in Figure 4. The raw materials used to fabricate the alloys are listed in Tables I and II.

Approximately four pounds of powder were processed for each of the alloys.

The procedures used to prepare the alloys was as follows:

(a) Nickel oxide and molybdenum dioxide were comminuted by attrition grinding in isopropyl alcohol to 0.1-0.2 microns as measured by electron microscopy techniques. Forty and sixty-three hours of grinding, respectively, were required to achieve the desired size. All comminution was performed in an all-nickel component system.

(b) Appropriate quantities of these oxides were dried and mixed such that the matrix material (after reduction) would contain 85% nickel and 15% molybdenum. Those powders to which alumina was later added were mixed in a Waring Blender; those to which thoria was added were blended by hand.

(c) Dispersoids at 2, 5 and 7.5 % were introduced into the matrix powder.

(1) Alumina by mechanical mixing in a Waring Blender in approximately 1/2 pound lots for 15 minutes.

(2) Thoria by decomposition of thorium nitrate. The matrix oxides (6-7 lbs.) were added to a methyl alcohol solution (about 1 liter) of the nitrate; mixing at ambient temperature in a household mixer was continued until the bulk of the alcohol was evaporated; the mixture was then allowed to stand in ceramic trays at ambient temperature to permit additional evaporation of the alcohol. The decomposition

was achieved by heating in a horizontal tube on ceramic trays in argon at 480° C (900° F) at a rate of 260° C (500° F) per hour. The product was then cooled to room temperature and stored in a desiccator.

(d) The matrix oxides were then reduced in a horizontal tube furnace by hydrogen at 1100° C (2010° F) for 5 hours. (Hydrogen flow 4 CFH.) The powders (100 grams per tube) were in low density nickel boats during the reduction. The powders were then stored in plastic bags contained in plastic containers in the dry box. The materials were never exposed to air after the reduction step. All processing steps for both the thoria and alumina-containing alloys were identical after the addition of these oxides to the matrix oxides had been effected.

(e) The powders were then placed in rubber-sleeved perforated metal cans. The powders were isostatically pressed at 30,000 psi. The densities and dimensions of the compacted billets are included in Table VII. The powders compacted to about 60% of theoretical density.

(f) The billets were canned in mild steel extrusion cans with evacuation tubes on both ends. These tubes were 1/2" O.D. (3/8" I.D.) by 3 feet long.

The extrusion cans had O.D.'s of 3.5".

(g) Hydrogen at 1100° C (2010° F) was passed through the cans for 5 hours. The cans were cooled to room temperature and one evacuation tube was closed.

(h) The cans were then evacuated at <0.01 microns at 538° C (1000° F) and subsequently sealed.

(i) The billets were extruded at 1093° C (2000° F) with an extrusion ratio of 12:1. Other pertinent extrusion variables are recorded in Table VIII. A photograph of the extruded alloys is given in Figure 5.

IV. EVALUATION OF EXTRUDED ALLOYS

1. Density

Density measurements of the extruded alloys were made by the water displacement technique. All materials had densities 99%

of theoretical except the two high aluminum oxide-containing alloys which had slightly lower densities. The data are recorded in Table IX.

2. Chemical Analysis

The results of the chemical analysis are recorded in Table X. It is apparent that contamination due to silicon, sulphur, carbon, and phosphorus is very low. Oxygen analyses by vacuum fusion indicate in all cases lower oxygen contents than are theoretically present due to deliberately added oxide dispersoids. It would be of great value to develop methods of chemical analyses which yield meaningful and quantitative results. With the techniques used at the present time, oxygen analysis can be used for comparative purposes only.

3. Structural Analysis

The microstructures of all the extruded alloys were examined by optical and electron optical techniques on longitudinal and transverse sections representing front, middle and tail of each extrusion. Representative pictures were made of all these sections at magnifications of 100X, 1000X and 20,000X. (The electron micrographs were taken at 5000X and subsequently enlarged to 20,000X.) All samples were etched chemically in a solution of 10% sodium cyanide and 10% ammonium persulfate in water. The etching time varied from seconds to several minutes, depending on the individual sample.

Figures 6-26 illustrate typical microstructures taken from longitudinal sections of the middle of all seven extrusions. (Following each of the 20,000X electron micrographs is included a picture of the same section taken after a 100-hour exposure at 1093° C (2000° F) in vacuum.) The photomicrographs of the material with no dispersoid (Figures 6-8) show a rather clean and nearly fully recrystallized structure with a grain size of 5-30 microns. The electron micrograph reveals a very fine substructure which does not disappear after 2000° F treatment and for this reason cannot be associated with cold work. (Figures 7-8) It would appear that this substructure might be associated with an ordering process in the nickel/molybdenum system. An x-ray pattern did, indeed, show some weak and rather blurred diffraction lines, which could not be associated with the nickel solid solution pattern. The same substructure cannot be seen in all alloys.

The photomicrographs of the thoria-containing alloys show a very fine dispersion which cannot readily be resolved by light microscopy. Some stringing can be observed with higher thoria content as can be seen in Figure 21 (7.5 V/o ThO₂). On the basis of the electron microscopic evidence, the thoria particle size is in the range of 0.05-0.5 microns, but the vast majority of the particles are smaller than 0.2 micron. It should also be kept in mind that particles smaller than 0.05 microns are probably present but cannot be resolved by the techniques used here. The distribution of the thoria particles is rather uniform and only a few clusters of second-phase particles can be observed.

The alumina-containing alloys, on the other hand, have a much more uneven structure. Both the 5 and the 7.5 V/o alumina alloys show heavy stringing and agglomeration of oxide particles. The 2 V/o alumina alloy (#3) has by far the most uniform structure of the three, but it is still inferior to the thoria-containing alloys in both oxide particle size and uniformity.

Microstructures of transverse sections are illustrated in Figures 27 and 28, representing alloy #2 (2 V/o ThO₂) and alloy #7 (7.5 V/o Al₂O₃). There is some evidence of inhomogeneities, possibly due to incomplete alloying; although it should be kept in mind that x-ray diffraction showed no indication of the molybdenum-rich phases.

A quantitative analysis was performed on the basis of electron micrographs taken on longitudinal sections from the center of the extrusion. Four different pictures per alloy were used, each comprising 100 square microns. The particles were sized within the observed range of 0.05 to 0.5 micron. The results are represented in the particle size distribution curves of Figures 31-36. With the exception of alloy #3 (2 V/o Al₂O₃) 1000-2000 individual particles per material were included; about 500 particles were included with this alloy.

Most distribution curves show no maximum within the particle size range evaluated, but rather increasing numbers with decreasing particle size. This observation is most accentuated in the low oxide content thoria alloys, and obviously it suggests that smaller particles are present.

In Table XI are listed the oxide contents and interparticle spacings as calculated on the basis of quantitative metallography (electron micrograph). It is assumed that the polished and etched planes included for the measurement and the counting of the particles are representative for a given alloy, which is undoubtedly an over simplification. As mentioned before, particles below a size of 0.05 micron were not included in the evaluation. This limitation is bound to affect the results because the particle size distribution curves very definitely suggest the presence of smaller particles. It is for this and other reasons that the numbers listed for average interparticle spacing appear to be too high. The formulas used have various additional limitations. One of them is the assumption that the oxide particles were uniformly distributed throughout the metal matrix*.

It is of interest to note that the calculated oxide volume percent data are in general rather close to the nominal ones. (Alloy #3 is somewhat of an exception.) It can be expected that two major sources of error are introduced in this calculation: The very small particles are not included, but, on the other hand, all the particles that were counted probably appear somewhat larger than their real size because of the etching effect.

4. Thermal Stability

Samples of all alloys were subjected to a heat treatment for 100 hours at 1093° C (2000° F) in vacuum (10^{-5} mm Hg). This type of a test has to be considered an extremely important one for an oxide dispersion-strengthened alloy, because only with thermal stability can one expect the desired benefit of this type of a structure.

*The authors have set up a computer program using X/Y coordinates of the center of the oxide particles in arbitrarily chosen planes. With this input one can expect to obtain a more realistic picture of the relative distances between neighboring particles. The aim is to get a range of distances between nearest neighbors.

After the heat treatment, alloys #2-7 were evaluated in the same manner as before. The results are represented in the particle size distribution curves as well as in Table XI. A typical electron micrograph is included for each alloy (Figures 8, 11, 14, 17, 20, 23, 26). All results indicate that the low oxide content alloys are rather stable. The 5 and the 7.5 V/o alumina-containing materials show considerable agglomeration which is illustrated rather well by both the electron micrographs and the oxide particle distribution curves. (See also Figure 30.)

The thoria alloys are in general more stable than the alumina alloys, although the microstructure of alloy #6 (7.5 V/o ThO_2) shows some void formation after the heat treatment; this is probably an indication for incomplete decomposition of the thoria salt prior to final consolidation. (Figure 29.)

The degree of stability of the various structures is well illustrated by hardness data before and after the heat treatment, as shown in Table XII. The data show that all materials have retained some cold work after extrusion. After the heat treatment, the hardness level stays about the same in all thoria-containing alloys and the 2 V/o alumina alloy. The highest alumina alloy shows a very drastic decrease in hardness whereas the 5 V/o alumina sample dropped by a few points.

It is of great value to note that simple hardness data can give a good indication of the thermal stability of a structure.

V. GENERAL CONCLUSIONS AND RECOMMENDATIONS FOR THE
EVALUATION OF MECHANICAL PROPERTIES

On the basis of the examination of the microstructures (100X, 1000X, 20000X) before and after a 1093° C (2000° F) stability test it was concluded that all thoria alloys and the 2 ^V/o alumina alloy represent attractive materials for further evaluation. This conclusion was made mostly on the basis of oxide particle size uniformity of the microstructure and thermal stability.

It was found that the currently used formulas for the calculation of the average interparticle spacing can be very useful for comparison purposes, but they are somewhat inadequate for the quantitative definition of the structure.

A recommendation was made for the evaluation of the high temperature stress rupture properties of the 2 and 5 ^V/o thoria alloys and the 2 ^V/o alumina alloy.

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3. "Process for Producing Sintered Metals with Dispersed Oxides", U.S. Patent 3,019,103 assigned to E.I. duPont deNemours and Company, January 30, 1962.
4. Fraser, R. W., Meddings, B., Evans, D.J.I. and Mackiw, V. N., "Dispersion Strengthened Nickel by Compaction and Rolling of Powder Produced by Pressure Hydrometallurgy", Preprint of paper presented at 1965 International Powder Metallurgy Conference, New York, June 14-17, 1965.
5. Pelloux, R.M.N. and Grant, N.J., "Solid Solution and Second Phase Strengthening of Nickel Alloys at High and Low Temperatures", Trans. A.I.M.E. 218, P. 233 (1960).
6. Rasmussen, J. G. and Grant, N. J., "Thoria Dispersion Strengthened Nickel and Nickel-Molybdenum Alloys Produced by Selective Reduction", Powder Metallurgy No. 14, 1964.

TABLE I: Raw Materials

<u>Material</u>	<u>Purity (%)</u>	<u>Size (Microns)</u>	<u>Supplier</u>
Nickel Oxide	99.9	0.6	Fisher Scientific Co. N-69
Molybdenum Dioxide	99.95 ⁽¹⁾	8.0	Climax Molybdenum Co.
Thorium Nitrate	99.9	-	Fisher Scientific Co. T-112
Aluminum Oxide	-	0.03	G. L. Cabot Co. Alon C

(1) 99.9% Molybdenum Trioxide reduced to the dioxide by Climax Molybdenum Co.

TABLE II: Emission Spectrographic Analyses
of as Received Matrix Oxide Powders

<u>Element</u>	<u>Nickel Oxide</u>	<u>Molybdenum Dioxide</u>
Nickel	>10%	<3 ppm
Molybdenum	-	>10%
Iron	0.03 - 0.3%	<3 ppm
Chromium	0.01 - 0.1	-
Magnesium	3 - 30 ppm	1 - 10 ppm
Copper	3 - 30 ppm	<3 ppm
Manganese	3 - 30 ppm	-
Silicon	3 - 30 ppm	1 - 10 ppm
Calcium	1 - 10 ppm	1 - 10 ppm

TABLE III: Analyses by Spectrographic Analysis of Powders
Comminuted in a Stainless Steel Attritor

<u>Element</u>	<u>Nickel Oxide</u>	<u>Molybdenum Dioxide</u>
Nickel	>10%	0.1 - 1%
Molybdenum	0.003 - 0.03	>10%
Iron	1 - 10%	1 - 10%
Chromium	0.3 - 3%	0.1 - 1%
Magnesium	0.003 - 0.03%	1 - 10 ppm
Copper	0.003 - 0.03%	0.001 - 0.01%
Manganese	0.01 - 0.1%	0.003 - 0.03%
Silicon	0.01 - 0.1%	0.01 - 0.1%
Calcium	1 - 10 ppm	<3 ppm
Cobalt	0.001 - 0.01%	0.001 - 0.01%
Silver	<3 ppm	<3 ppm
Aluminum	0.001 - 0.01%	-
Boron	3 - 30 ppm	-
Vanadium	3 - 30 ppm	1 - 10 ppm

TABLE IV: Effect of Time, Temperature and Atmosphere on
Crystal Size of Thorium Oxide Prepared by
Decomposition of Thorium Nitrate

Crystal Size, Microns
Using The Indicated Atmosphere

<u>Temperature</u> <u>(°C)</u>	<u>Argon</u>	<u>Hydrogen</u>	<u>Vacuum</u>
<u>One Hour</u>			
480	<0.01	<0.01	<0.01
650	<0.01	0.01	<0.01
815	0.01	0.02	0.03
982	0.03	0.03	0.03
<u>Five Hours</u>			
480	<0.01	<0.01	0.01
650	0.01	0.01	0.02
815	0.02	0.02	0.03
982	0.03	0.04	0.03
<u>Fifteen Hours</u>			
480	-	-	-
650	<0.01	0.01	0.02
815	0.01	0.04	0.03
982	0.04	0.04	0.03

TABLE V: Oxygen Analyses and Thorium Oxide Crystal Size in Powder Mixtures After Hydrogen Treatment

Sample	Thorium Oxide V/o	Decomposition Temp. (°C)	Reduction Temp. (°C)	Reduction Time (hrs.)	One Hour Sinter Temp. (°C)	Percent Total Oxygen*	Thorium Oxide Crystal Size by x-ray diffraction (microns)
1A	0	-	1000	1	-	0.30	-
3A	0	-	1200	1	-	0.04	-
10	2.5	480	1100	5	1200	0.32	0.05
11	2.5	815	1100	5	1200	0.44	0.03
12	2.5	982	1100	5	1200	1.02	0.03
1	5.0	480	1000	1	1200	0.34	0.02
2	5.0	480	1100	1	1200	0.34	0.04
3	5.0	480	1200	1	1200	0.18	0.03
4	5.0	480	1000	5	1200	0.31	0.02
5	5.0	480	1100	5	1200	0.18	0.04
7	5.0	480	1100	5	1100	0.18	0.03
9	5.0	480	1100	5	1300	0.18	0.04
6	5.0	480	1200	5	1200	0.15	0.03
7A	5.0	815	1100	5	1100	-	0.02
8A	5.0	815	1100	5	1200	-	0.03
9A	5.0	815	1100	5	1300	-	0.04
13	7.5	480	1100	5	1200	0.49	0.05

*All oxygen analyses after reduction and before sintering

TABLE VI: Oxygen Analyses and Aluminum Oxide Crystal Size in Powder Mixtures After Hydrogen Treatment

<u>Sample</u>	<u>Reduction^a Temperature (°C)</u>	<u>Sinter^b Temperature (°C)</u>	<u>Percent^c Total Oxygen</u>	<u>Alpha Crystal^d Size (microns)</u>	<u>Gamma Crystal^d Size (microns)</u>
		<u>5 % Alpha Aluminum Oxide</u>			
101	1100	1200	0.22	0.03	-
102	1100	1300	0.22	0.02	-
103	1200	1200	0.23	0.03	-
		<u>5 % Gamma Aluminum Oxide</u>			
201	1100	1200	0.25	0.02	0.02
202	1100	1300	0.25	0.03	0.03
203	1200	1200	0.14	0.03	0.02

^a All reductions for 5 hours

^b All sinters for 1 hour

^c All oxygen analyses after reduction and before sintering

^d Measured after sintering by x-ray diffraction methods

TABLE VII; Data on Cold Compacted Alloys

<u>Alloy No.</u>	<u>Dispersoid</u>	<u>Density % Theoretical^a</u>	<u>Max. Billet Diameter, Inches</u>	<u>Max. Billet Height, Inches</u>
1	None	62	2.59	3.88
2	2.0 ^v /o ThO ₂	63	2.34	4.28
3	2.0 ^v /o Al ₂ O ₃	59	2.70	3.85
4	5.0 ^v /o ThO ₂	62	2.62	4.45
5	5.0 ^v /o Al ₂ O ₃	70	2.60	4.03
6	7.5 ^v /o ThO ₂	63	2.55	4.45
7	7.5 ^v /o Al ₂ O ₃	74	2.47	3.83

^aAverage dimensions of the billets
were used to calculate the densities.

TABLE VIII: Extrusion Variables in the Fabrication of
Nickel-15% Molybdenum Alloys

Can Material	Mild Steel
Extrusion Temperature, °F	2000
Die Size, Inches	1.00
Reduction Ratio	12:1
Extrusion Speed, Inches Per Minute	40
Heating Up Time, Hours	2 1/2
Liner Size, Inches	3 1/2
Lubrication	Mica
Evacuation Procedure	<0.01μ @1000°F
Transfer Time, Seconds	20
Die Angle	90° ^a
Condition of Core	Compacted Billets
Liner Temperature, °F	750
Press, Tons	1000

Other data are the following:

<u>Alloy No.</u>	<u>Maximum Force, Tons</u>	<u>Extrusion Constant, psi^b</u>
1	533	21.7
2	506	20.6
3	533	21.7
4	533	21.7
5	586	23.8
6	560	22.8
7	573	23.3

^aThe included angle that leads into the die opening, the size of which is determined by the reduction ratio desired.

^bThese data were obtained from $K = \frac{\text{Max. force to extrude, tons/sq. in.}}{\ln. \text{ reduction ratio}}$

TABLE IX: Density of Extruded Alloys^a

<u>Alloy No.</u>	<u>Dispersoid</u>	<u>Measured Density, g/cm³</u>	<u>Density, % of Theoretical</u>
1	None	9.11	100
2	2.0 ^v /o ThO ₂	9.11	99
3	2.0 ^v /o Al ₂ O ₃	8.97	99
4	5.0 ^v /o ThO ₂	9.14	99
5	5.0 ^v /o Al ₂ O ₃	8.73, 8.73 ^b	98
6	7.5 ^v /o ThO ₂	9.16	99
7	7.5 ^v /o Al ₂ O ₃	8.45, 8.45 ^b	97

^aBy water displacement techniques.

^bDuplicate determinations on different sections of alloys.

TABLE X: Chemical Analyses of Extruded Alloys
(weight percent)

<u>Alloy No.</u>	<u>Dispersoid</u>	<u>C^b</u>	<u>P^c</u>	<u>S^b</u>	<u>Si^c</u>	<u>N₂^a</u>	<u>O₂^a</u>	<u>H₂^a</u>
1	None	.014	.001	.001	.03	.0002	.0295	.0006
2	2.0 ^v / _o ThO ₂	.015	.001	.009	.01	.0022	.1855	.0001
3	2.0 ^v / _o Al ₂ O ₃	.016	.001	.010	.03	.0002	.2641	.0002
4	5.0 ^v / _o ThO ₂	.020	.001	.004	.02	.0005	.1118	.0001
5	5.0 ^v / _o Al ₂ O ₃	.016	.005	.009	.03	.0005	.4198	.0000
6	7.5 ^v / _o ThO ₂	.011	.001	.007	.02	.0005	.3436	.0005
7	7.5 ^v / _o Al ₂ O ₃	.012	.001	.009	.02	.0047	.4487	.0005

^a By vacuum fusion at 1800°C

^b Wet chemical - fusion techniques - Leco method

^c Wet chemical - ASTM procedures

TABLE XI: Calculated Volume Percent and Interparticle Spacing of Oxide Particles in Nickel-15% Molybdenum Alloys

<u>Alloy No.</u>	<u>Nominal Composition of Oxide Phase</u>	<u>Calculated Volume % of Oxide Phase of As Extruded Alloys</u>	<u>Interparticle Spacing^a of Oxide Particles of As Extruded Alloys, Microns</u>	<u>Interparticle Spacing^b of Oxide Particles of As Extruded Alloys, Microns</u>	<u>Interparticle Spacing^a of Oxide Particles of Heat Treated Alloys, Microns</u>
2	2.0 V/o ThO ₂	2.1	5.90	5.13	7.07
3	2.0 V/o Al ₂ O ₃	3.2	8.59	7.16	9.85
4	5.0 V/o ThO ₂	4.6	2.65	2.37	2.66
5	5.0 V/o Al ₂ O ₃	5.8	2.63	2.38	5.73
6	7.5 V/o ThO ₂	6.8	1.83	1.79	2.39
7	7.5 V/o Al ₂ O ₃	6.7	2.00	1.87	2.24

^aObtained from formula

$$\text{I.P.} = 4 \left(\frac{\sum V}{\sum S} \right)_{\text{ox}} \left(\frac{1}{f_{\text{ox}}} - 1 \right)$$

Where:

I.P. is the average interparticle spacing.

^bObtained from formula

$$\text{I.P.} = \left(\frac{\sum A}{\sum C} \right)_{\text{ox}} \left(\frac{1}{f_{\text{ox}}} - 1 \right)$$

$\left(\frac{\sum V}{\sum S} \right)_{\text{ox}}$ Represents ratio of volume to surface area for the dispersoid phase in a composite alloy.

$\left(\frac{\sum A}{\sum C} \right)$ Represents ratio of total measured two dimensional particle area to total measured particle boundary (measured on a random plane through the composite material).

f_{ox} Volume fraction of oxide.

TABLE XII: Hardness Values of Extruded Alloys
Before and After 2000° F Annealing Treatment

<u>Hardness Value - Rockwell A</u>			
<u>Alloy No.</u>	<u>Dispersoid</u>	<u>Before Heat Treatment</u>	<u>After Heat Treatment</u>
1	None	54.5	51.8
2	2.0 % ThO_2	61.9	60.5
3	2.0 % Al_2O_3	61.3	60.4
4	5.0 % ThO_2	65.8	64.5
5	5.0 % Al_2O_3	64.7	61.0
6	7.5 % ThO_2	65.7	66.0
7	7.5 % Al_2O_3	64.7	47.0

Values represent averages of at least 3 data points.

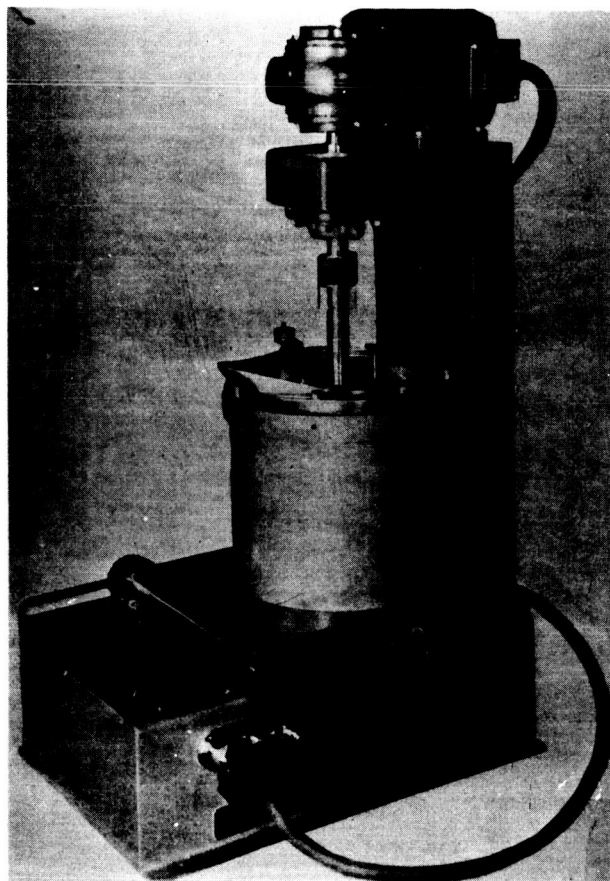
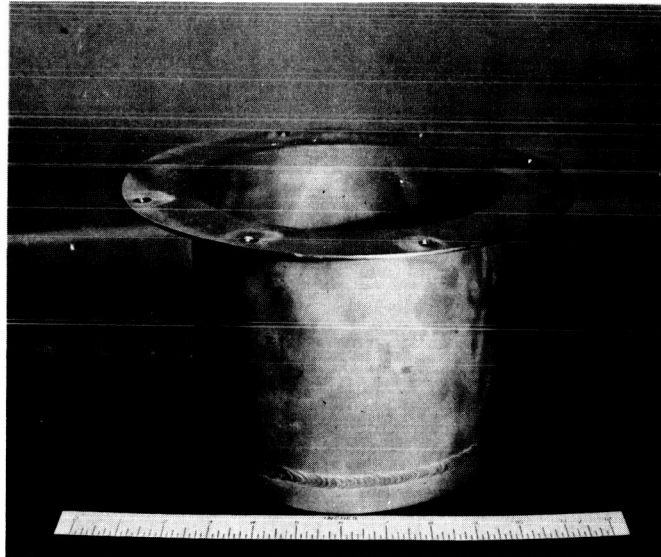
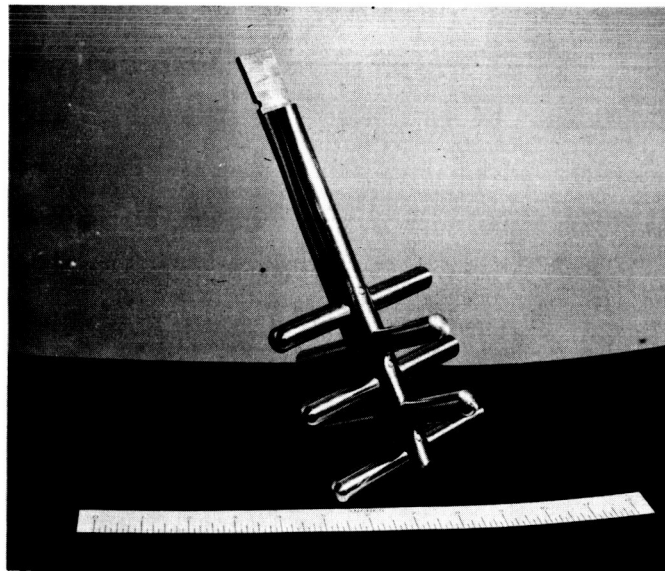


Figure 1: Attritor Grinding Unit.
(Model 1-S) Made by
Union Process Company,
Akron, Ohio

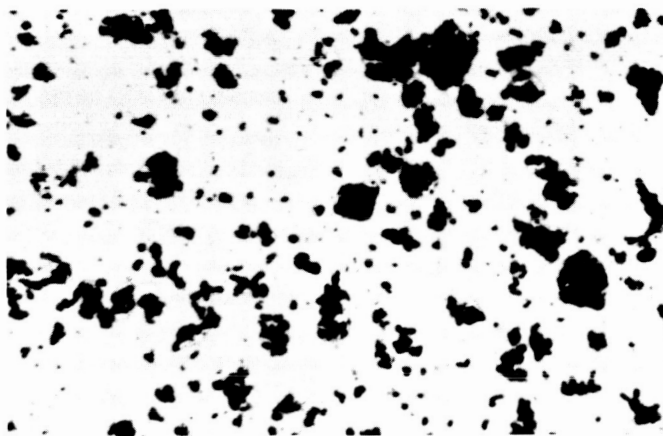


Attritor Grinding Tank

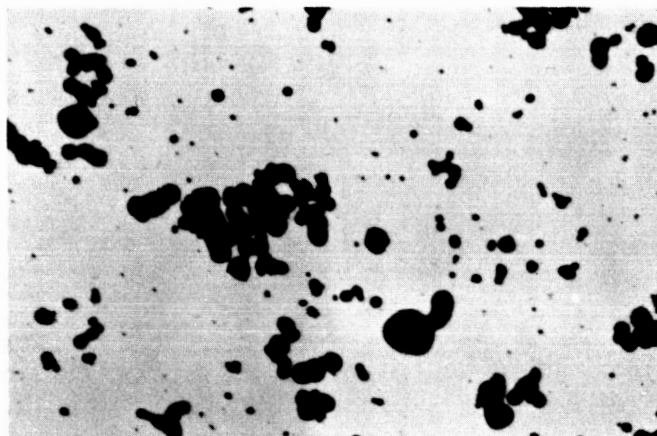


Attritor Grinding Spindle

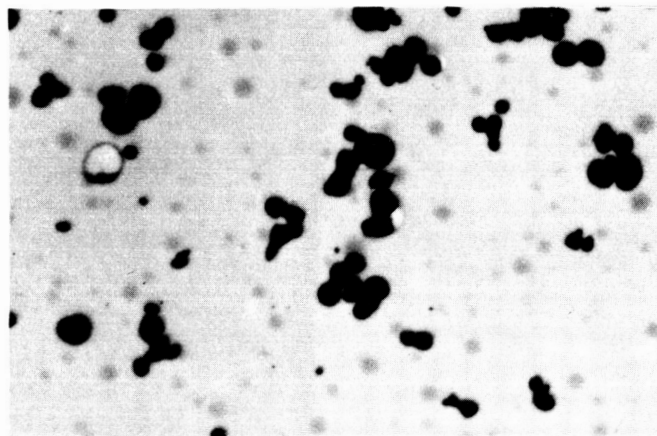
Figure 2: Attritor Components.



Sample 4, Table V, 5^V/o ThO₂, decomposed at 480° C reduced
5 hours at 1000° C, sintered 1 hour at 1200° C.



Sample 3, Table V, 5^V/o ThO₂, decomposed at 480° C reduced
1 hour at 1200° C, sintered 1 hour at 1200° C.



Sample 13, Table V, 7.5^V/o ThO₂, decomposed at 480° C reduced
5 hours at 1100° C, sintered 1 hour at 1200° C.

Figure 3: Extracted Thorium Oxide Particles.

10,000X

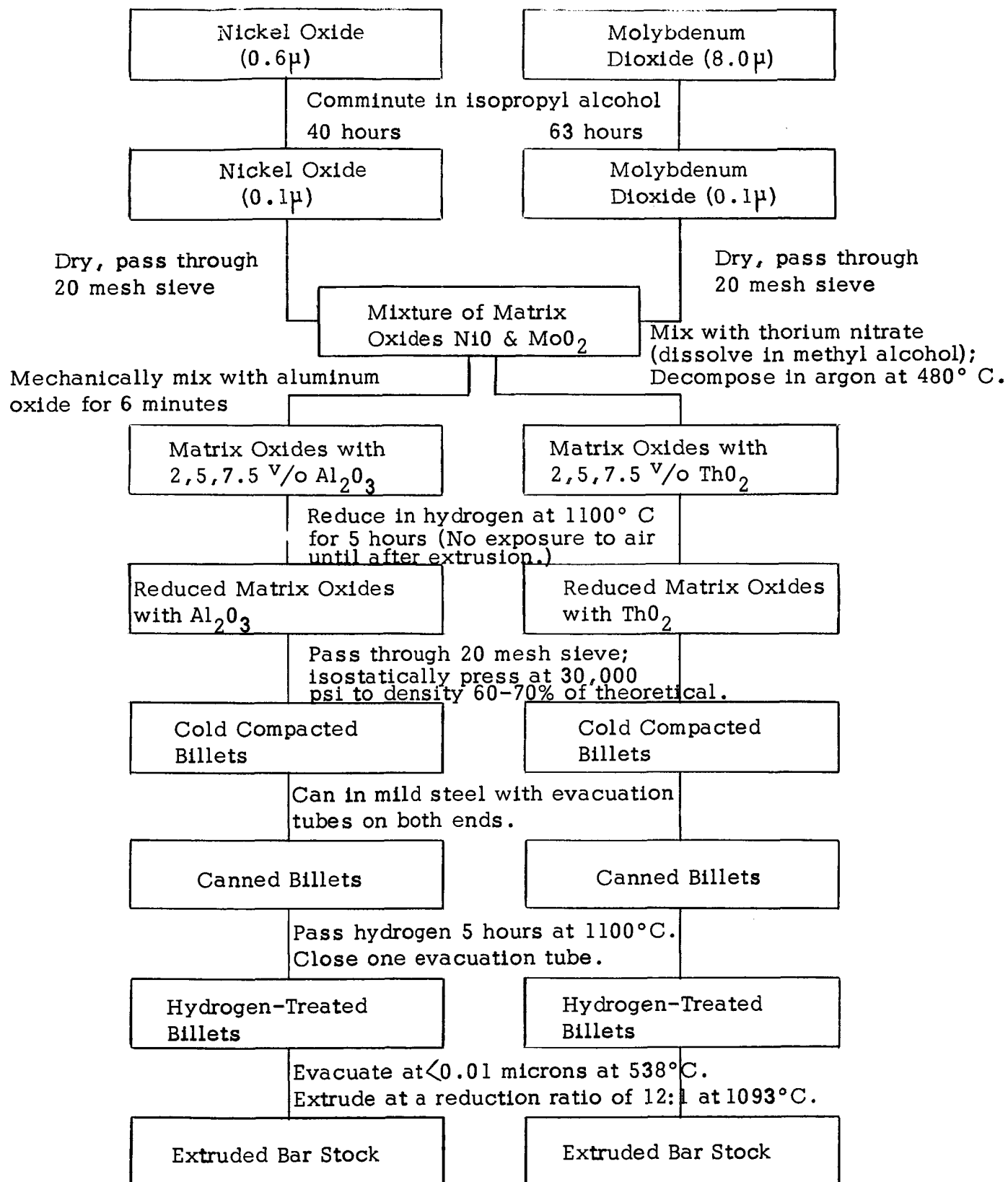


Figure 4: Processing Chart

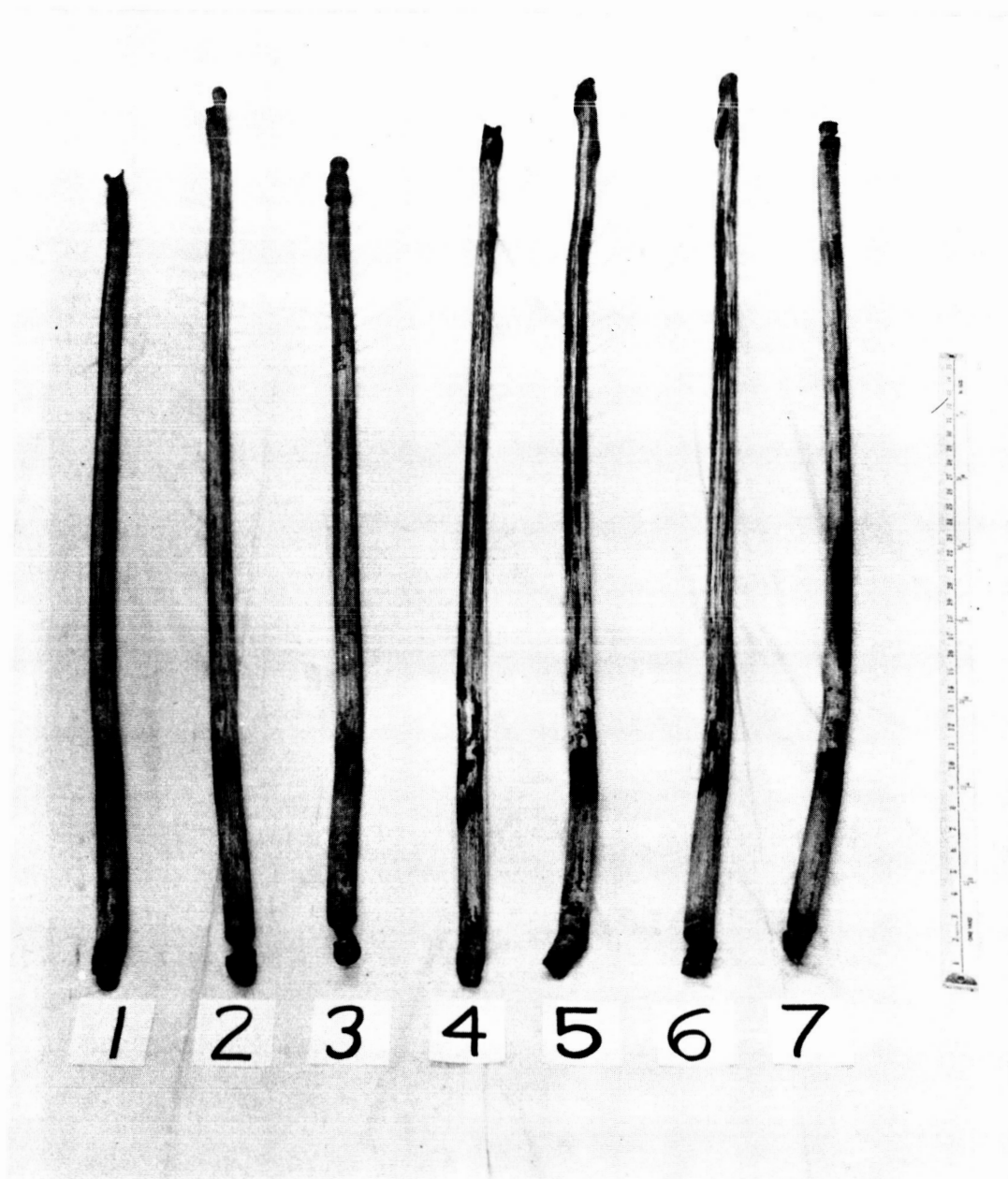
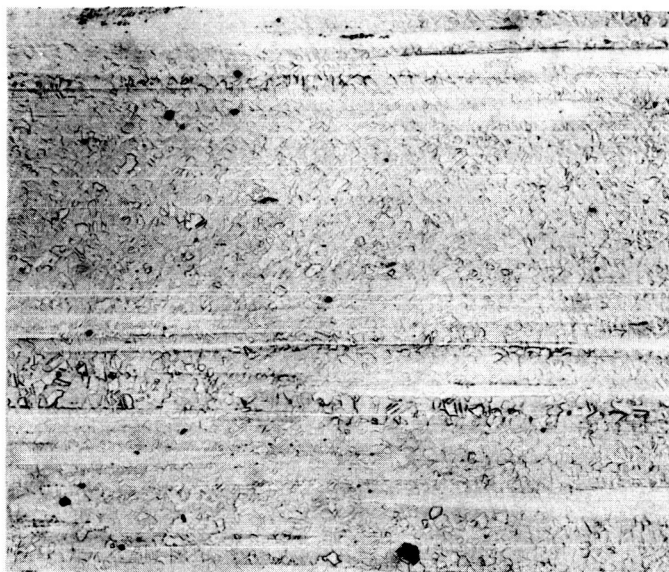


Figure 5: Photograph of Extruded Nickel/Molybdenum-Base Alloys.



100X



1000X

Figure 6: Microstructure of longitudinal section of alloy #1 (Ni-15% Mo) taken from the center of the extrusion.

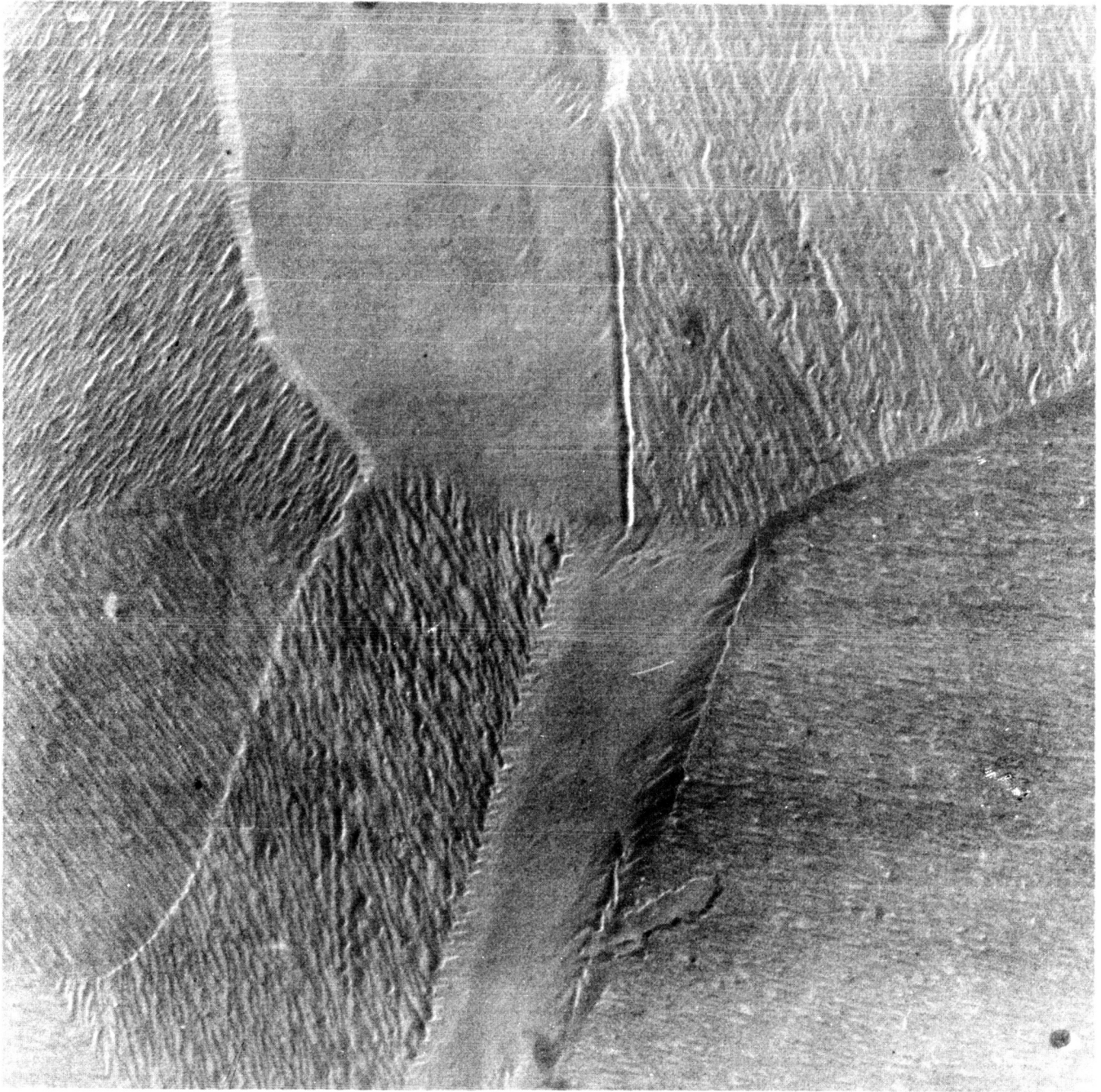


Figure 7: Electron micrograph of longitudinal section of alloy #1 (Ni-15% Mo) taken from the center of the extrusion. Etched, 20,000X

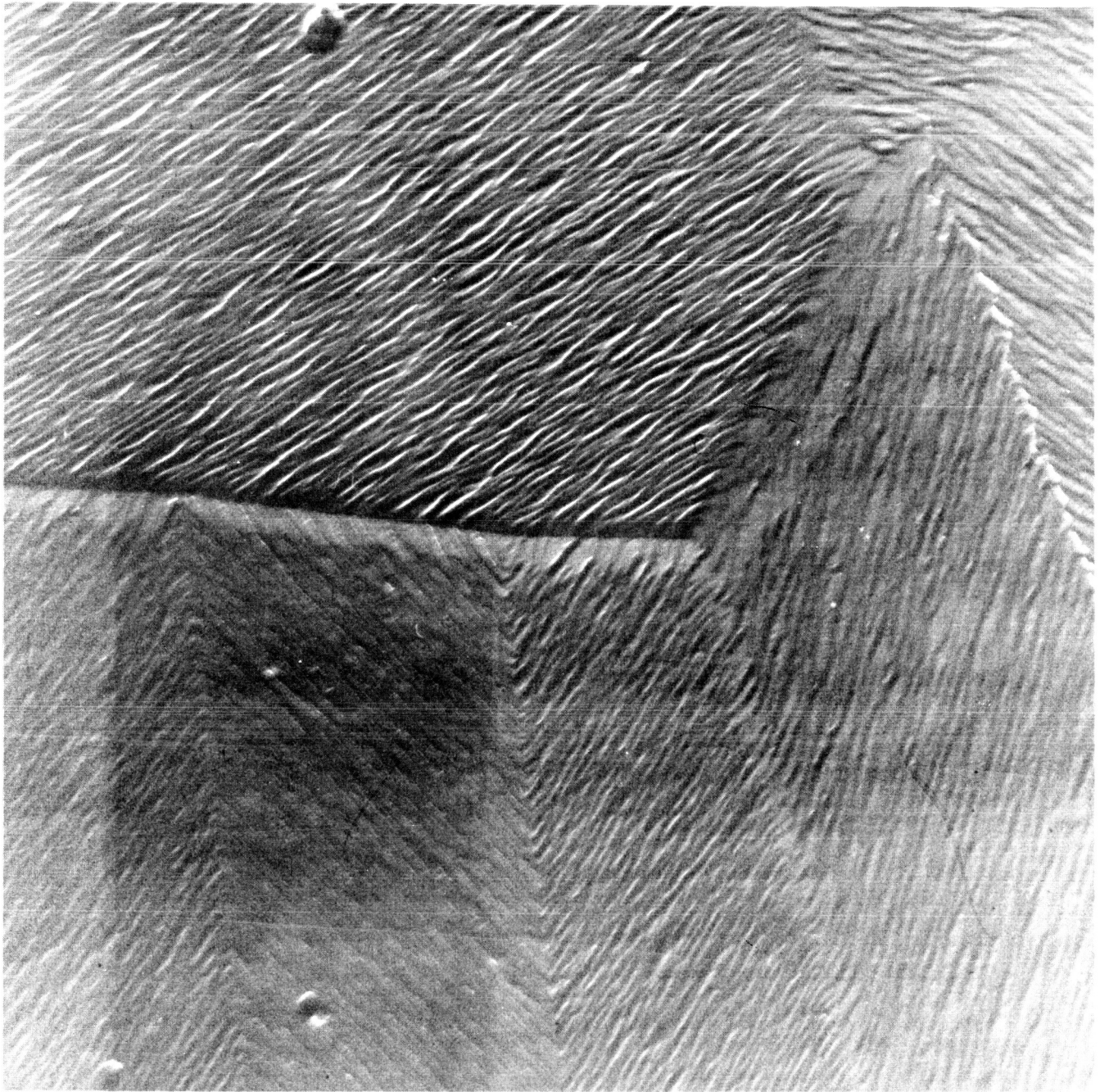
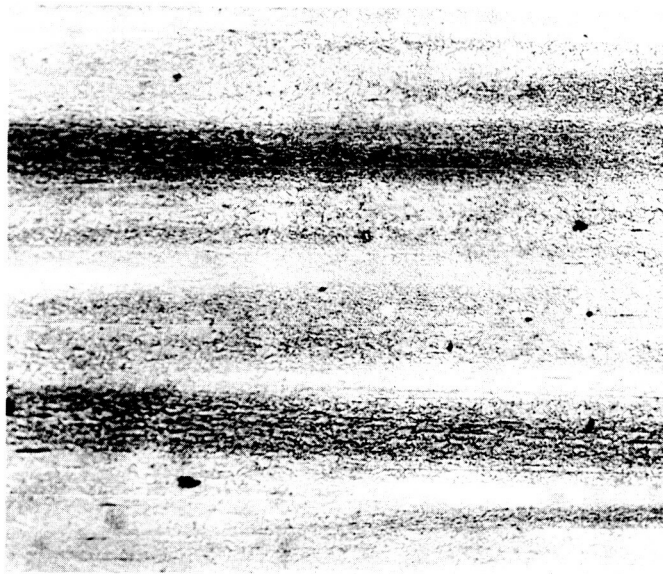
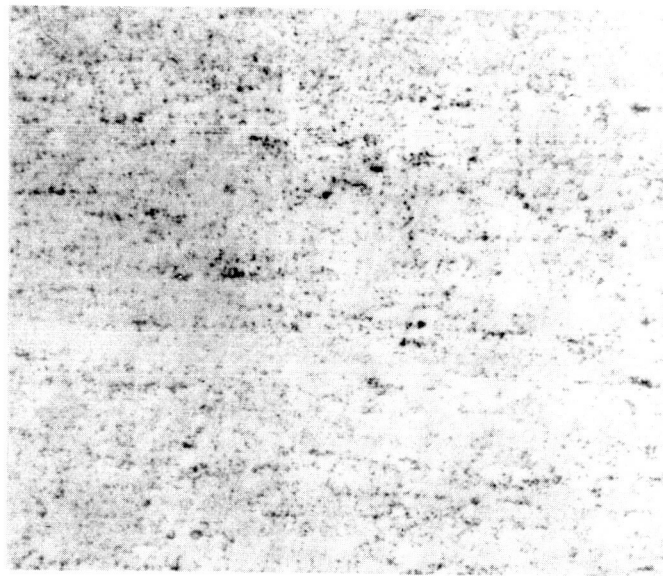


Figure 8: Electron micrograph of same section as Figure 7 after 100 hours at 2000° F
in vacuum (10^{-5} mm Hg). Etched, 20,000X



100X



1000X

Figure 9: Microstructure of longitudinal section of alloy #2 (Ni-15% Mo + 2 ^v/o ThO₂) taken from the center of the extrusion.

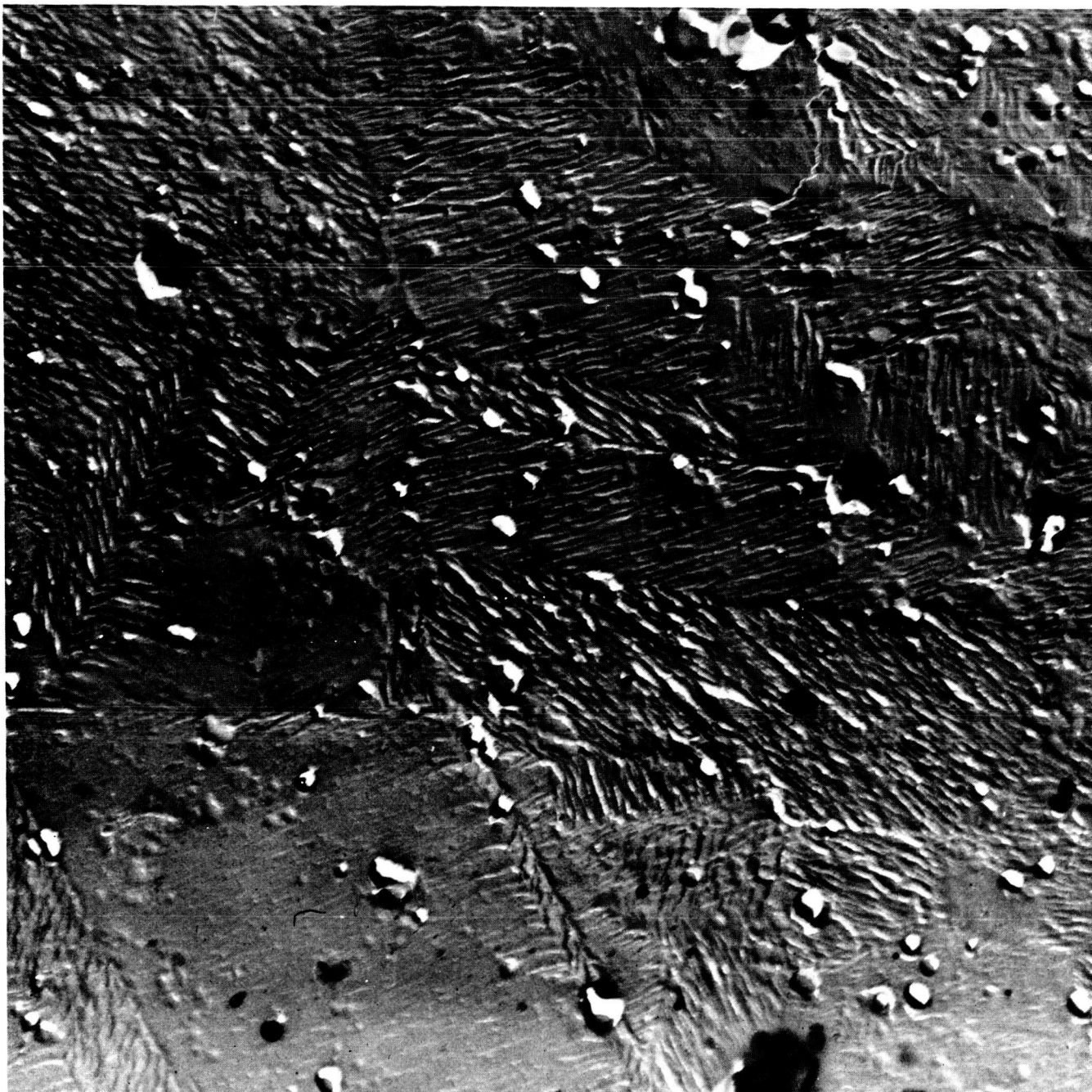


Figure 10: Electron micrograph of longitudinal section of alloy #2 (Ni-15% Mo + 2^V/o ThO₂) taken from the center of the extrusion. Etched, 20,000X

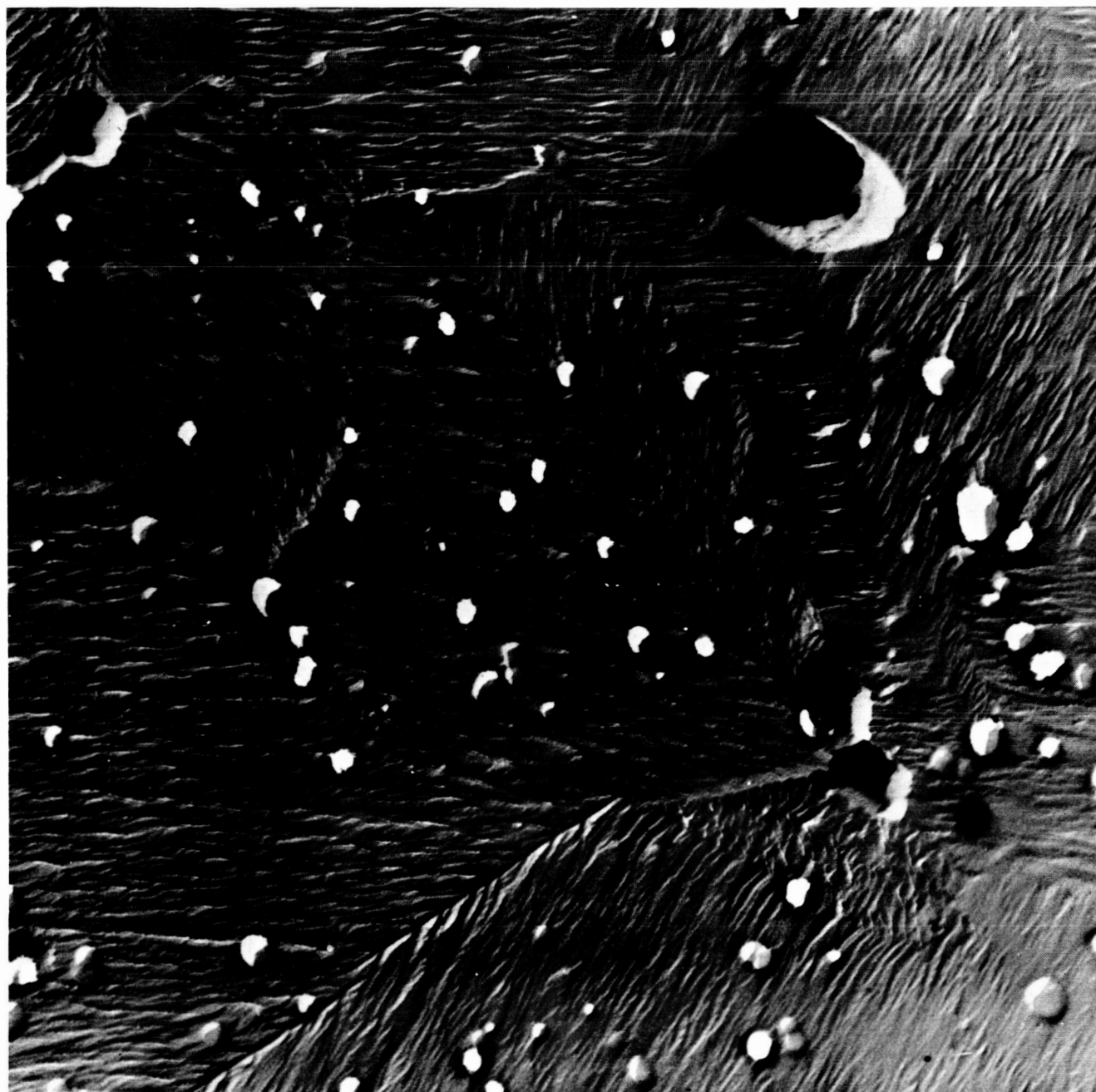
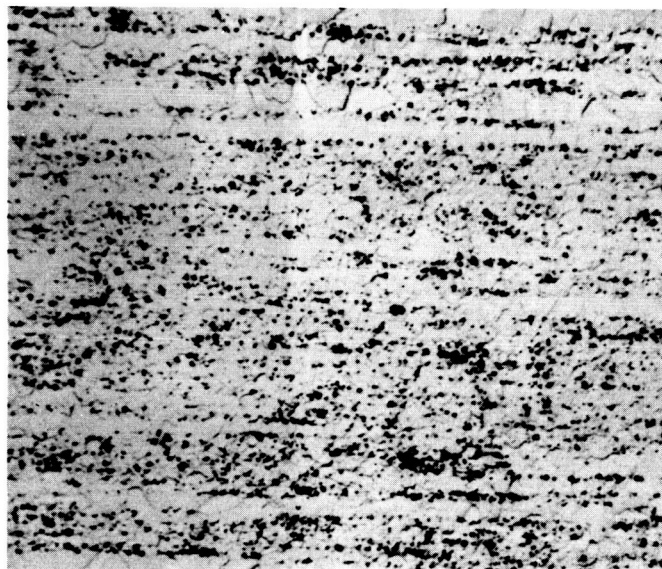


Figure 11: Electron micrograph of same section as Figure 10 after 100 hours at 2000° F
in vacuum (10^{-5} mm Hg). Etched, 20,000X



100X



1000X

Figure 12: Microstructure of longitudinal section of alloy # 3 (Ni-15% Mo + 2^v/o Al₂O₃) taken from the center of the extrusion.

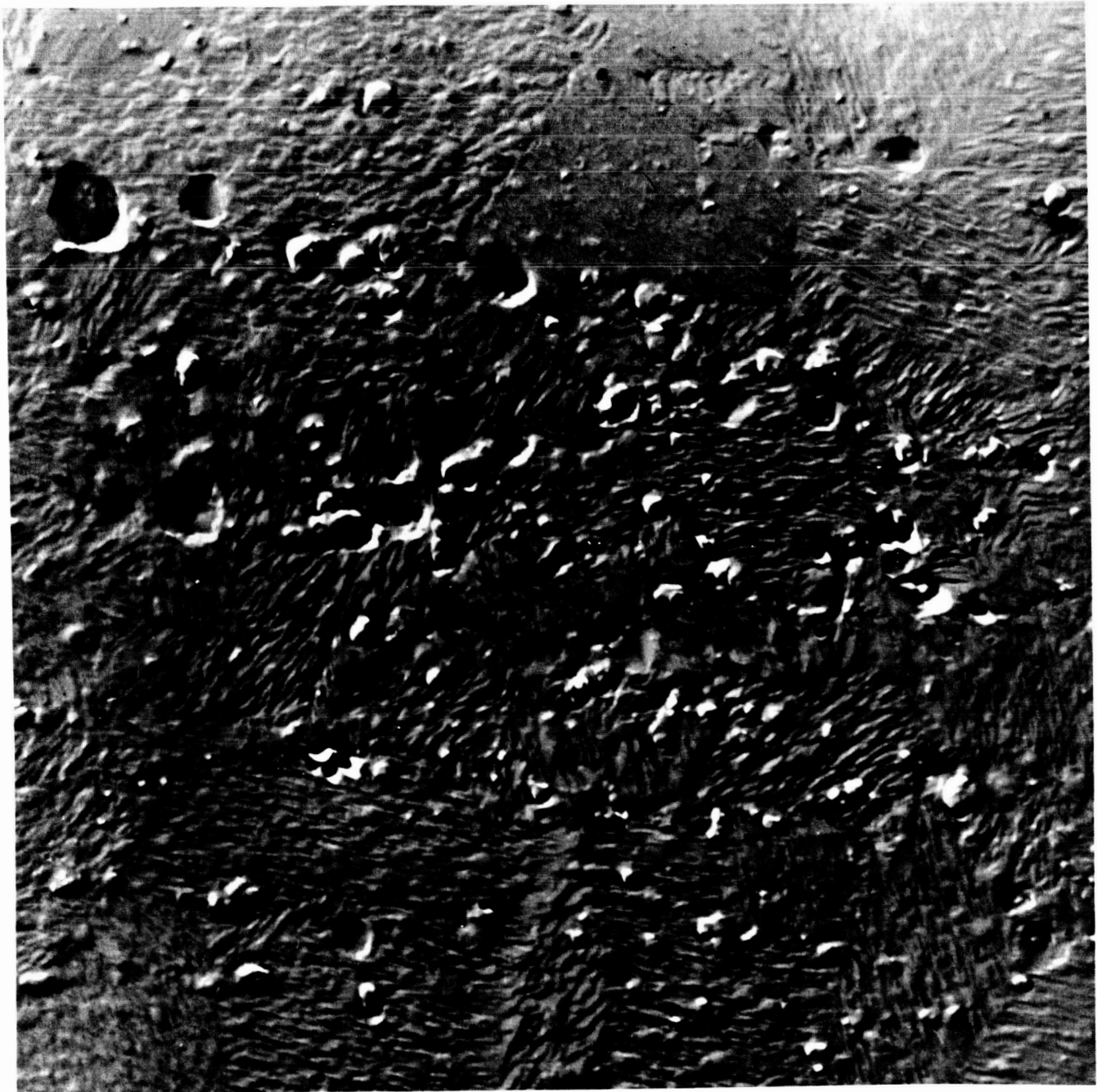


Figure 13: Electron micrograph of longitudinal section of alloy #3 (Ni-15% Mo + 2 V/o Al_2O_3) taken from the center of the extrusion. Etched, 20,000X

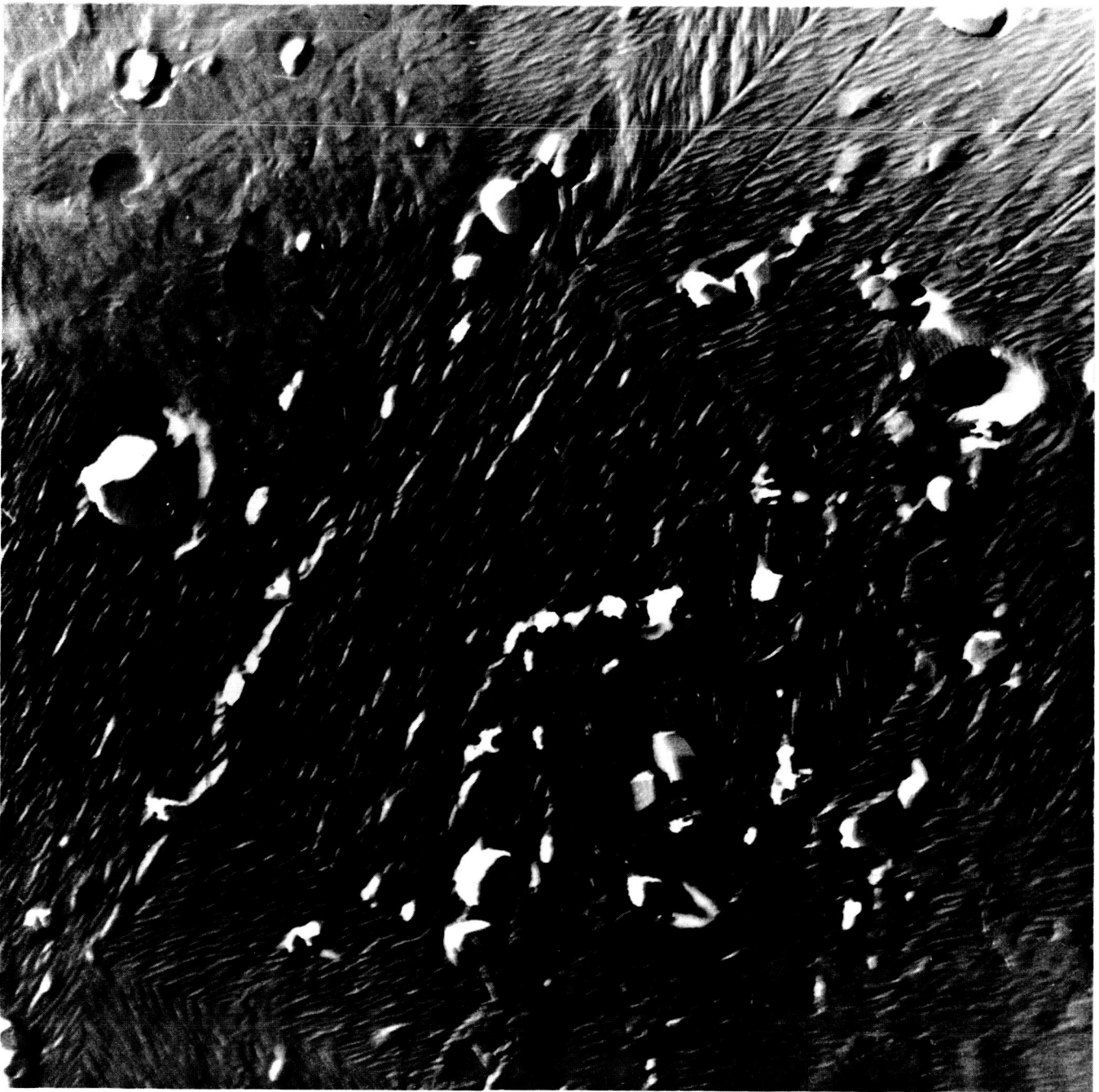
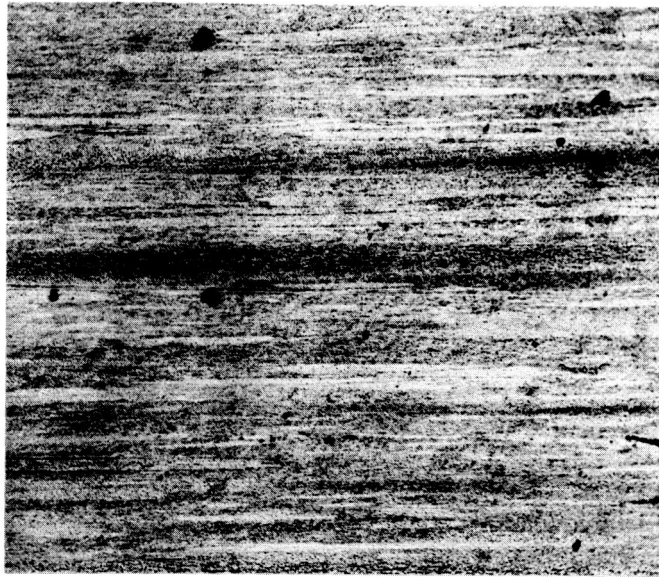
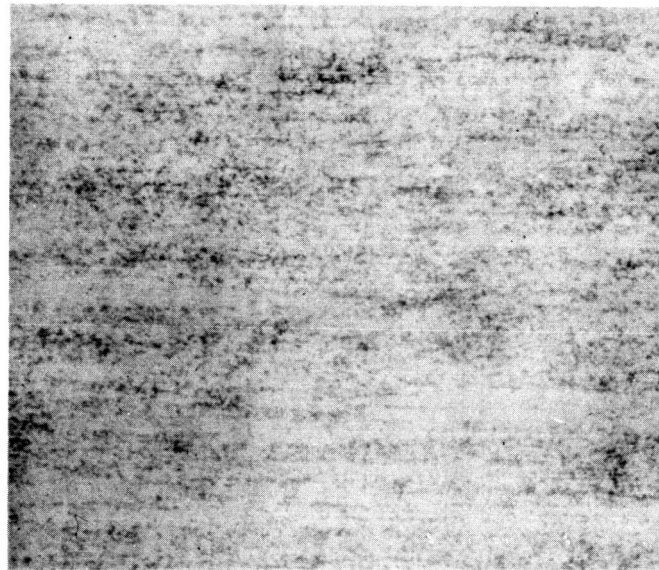


Figure 14: Electron micrograph of same section as Figure 13 after 100 hours at 2000° F
in vacuum (10^{-5} mm Hg). Etched, 20,000X



100X



1000X

Figure 15: Microstructure of longitudinal section of alloy #4 (Ni-15% Mo + 5 v/o ThO₂) taken from the center of the extrusion.

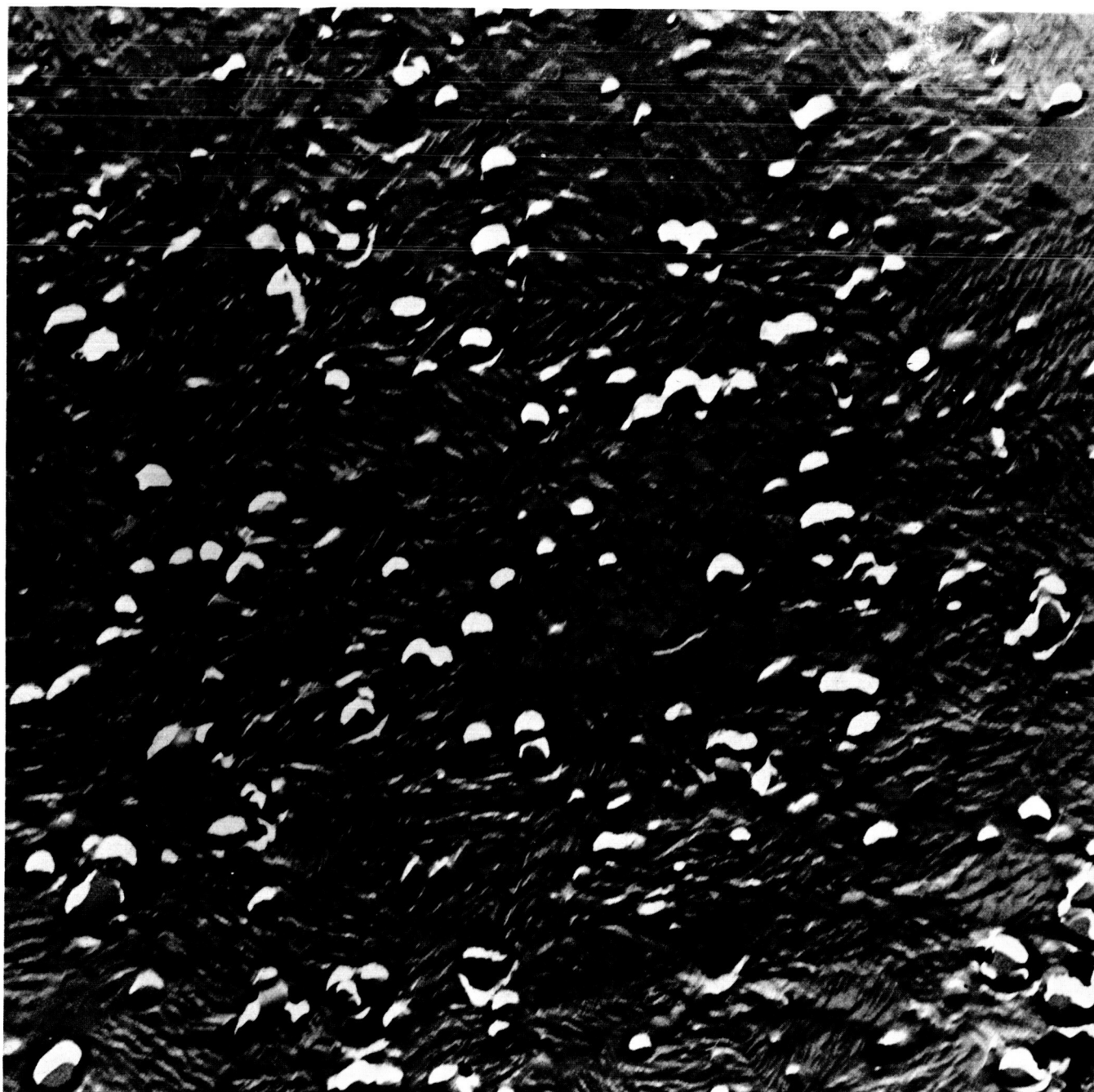


Figure 16: Electron micrograph of longitudinal section of alloy #4 (Ni- 15% Mo + 5 V/o ThO₂) taken from the center of the extrusion. Etched, 20,000X

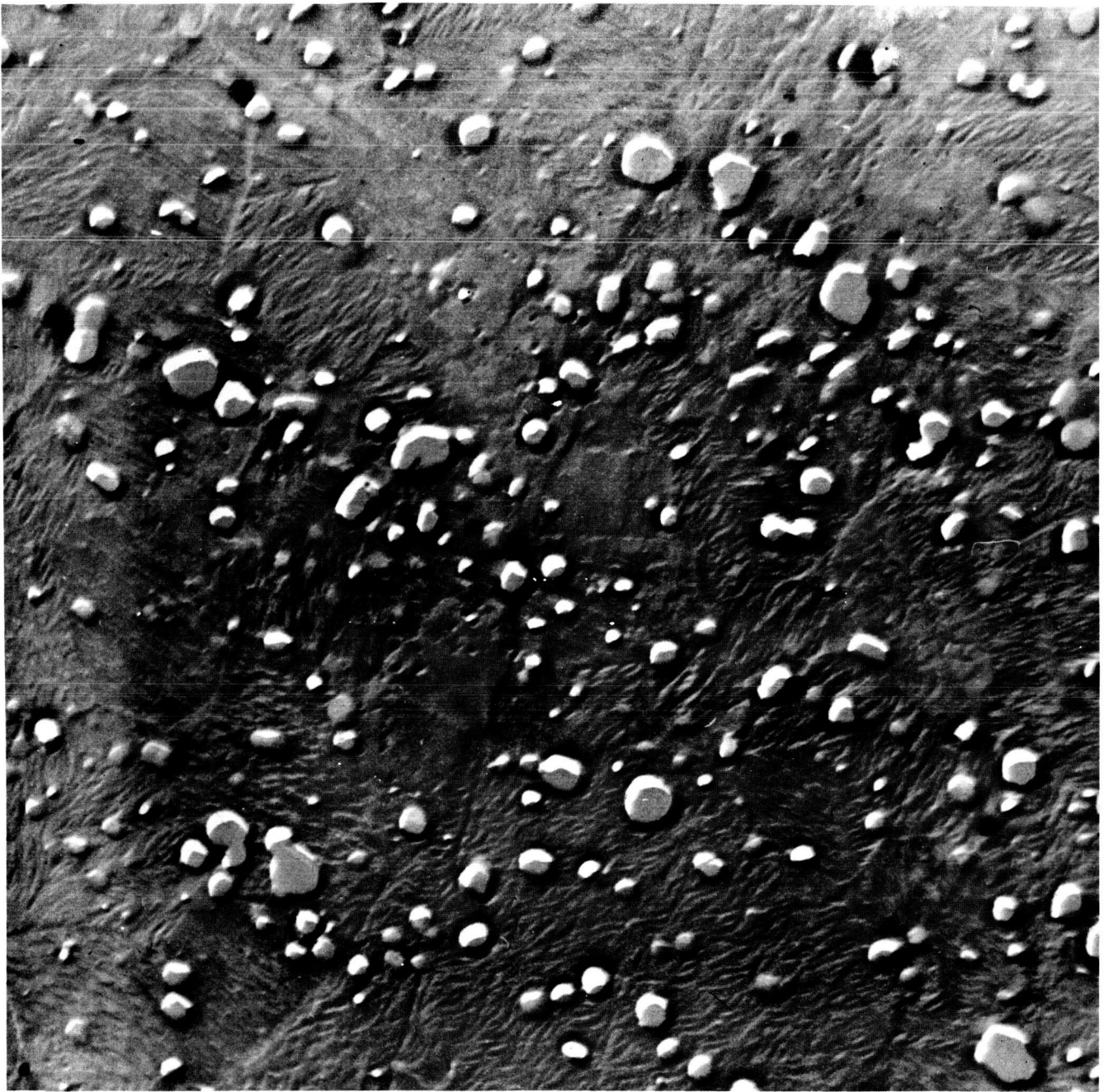
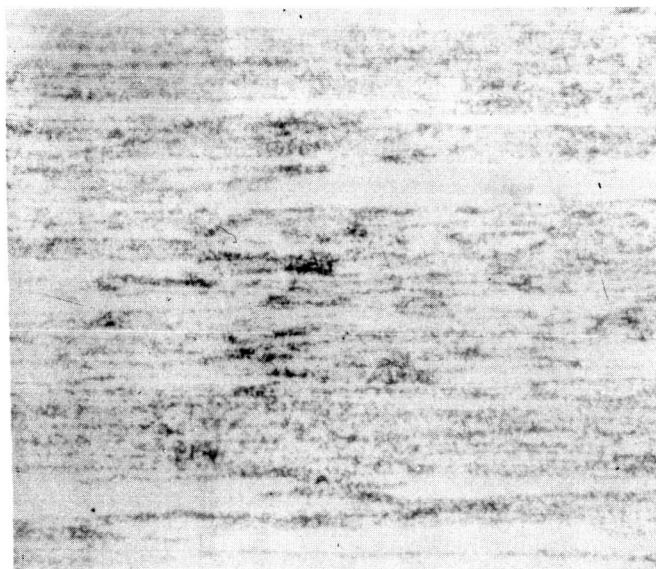


Figure 17: Electron micrograph of same section as Figure 16 after 100 hours at 2000° F
in vacuum (10^{-5} mm Hg) . Etched, 20,000X



100X



1000X

Figure 18: Microstructure of longitudinal section of alloy #5 (Ni-15% Mo+ 5^V/o Al₂O₃) taken from the center of the extrusion.

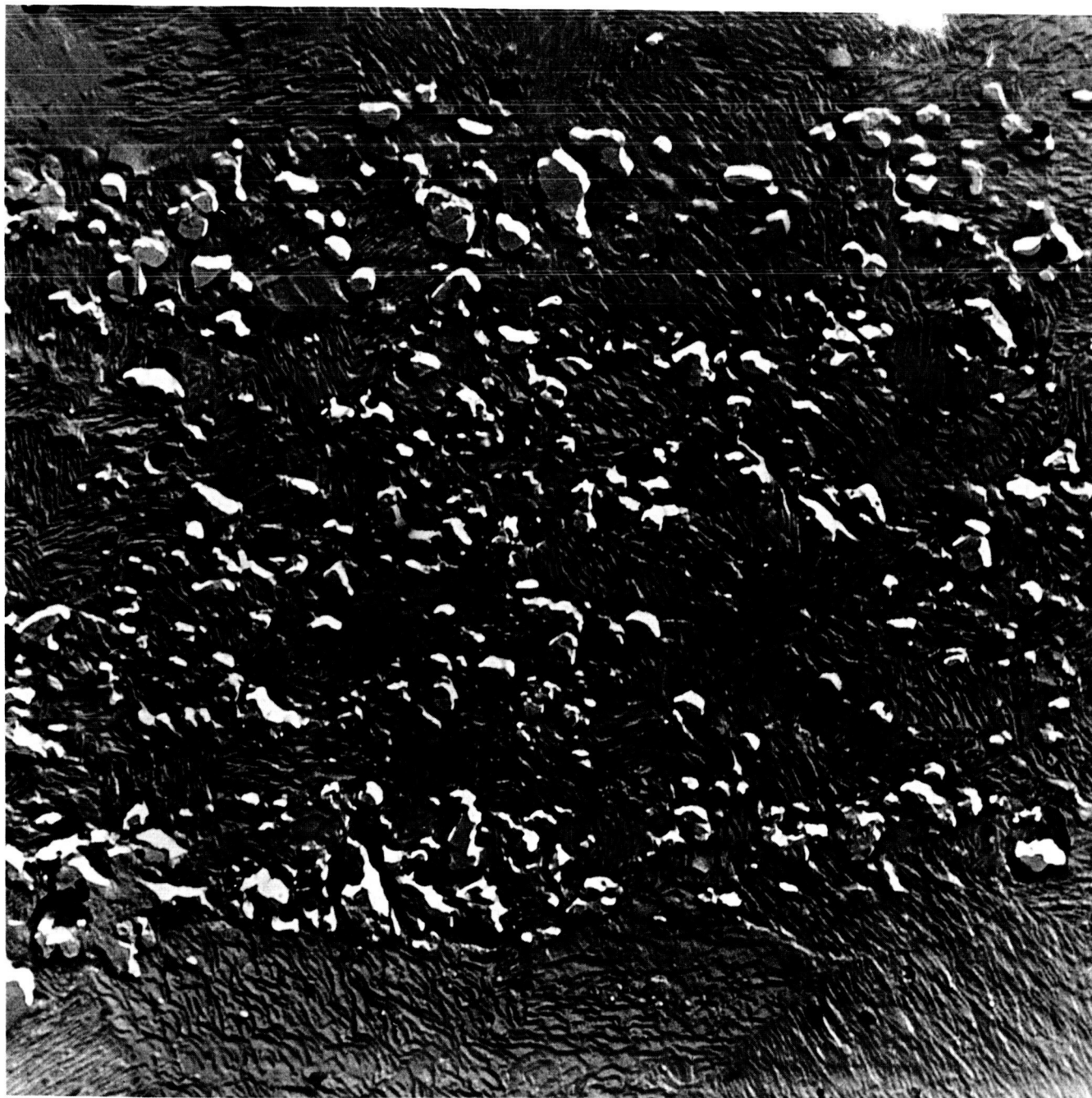


Figure 19: Electron micrograph of longitudinal section of alloy # 5 (Ni-15% Mo + 5 V/o Al₂O₃) taken from the center of the extrusion. Etched, 20,000X

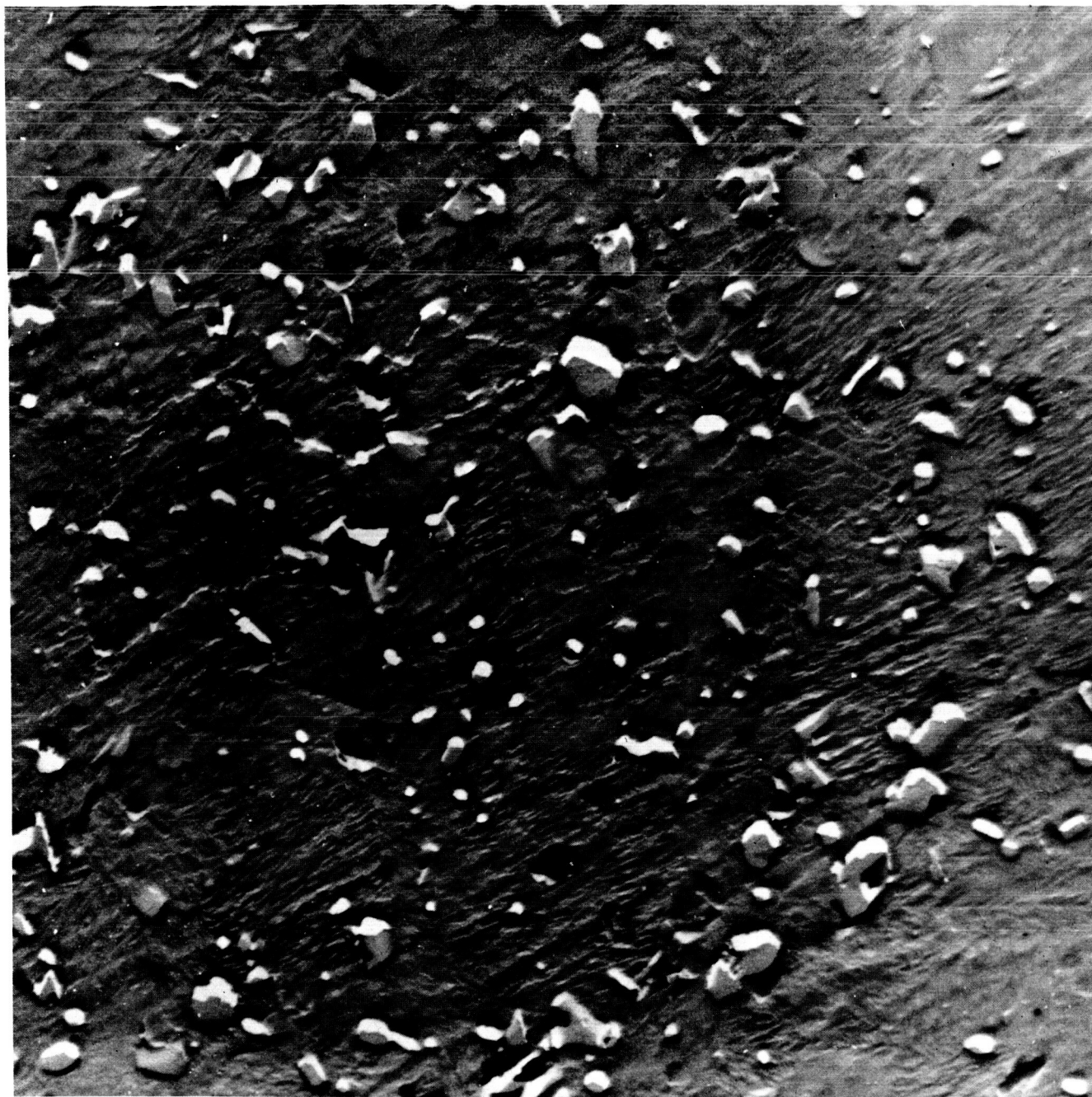
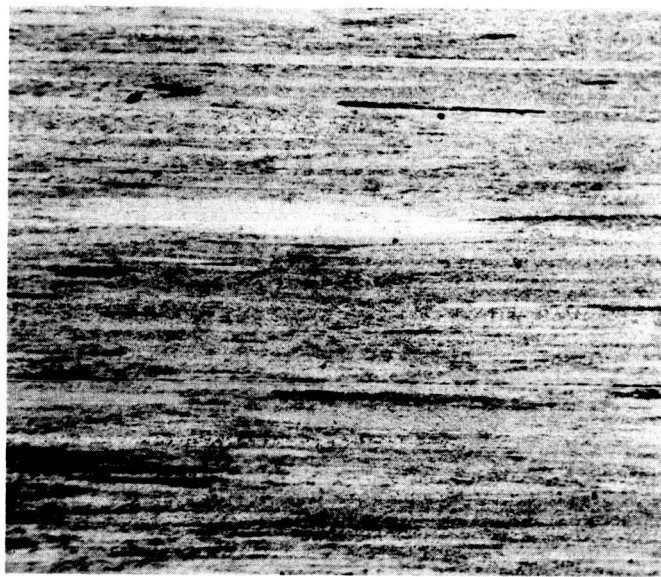
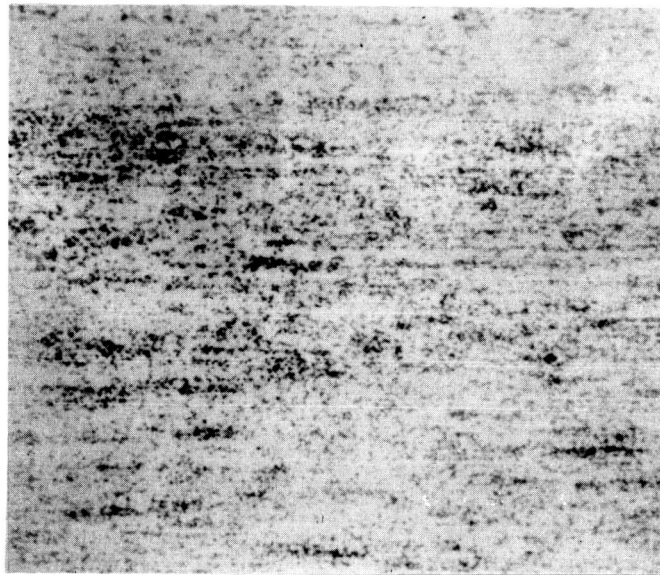


Figure 20: Electron micrograph of same section as Figure 19 after 100 hours at 2000° F
in vacuum (10^{-5} mm Hg). Etched, 20,000X



100X



1000X

Figure 21: Microstructure of longitudinal section of alloy #6 (Ni-15% Mo + 7.5 ^v/o ThO₂) taken from the center of the extrusion.

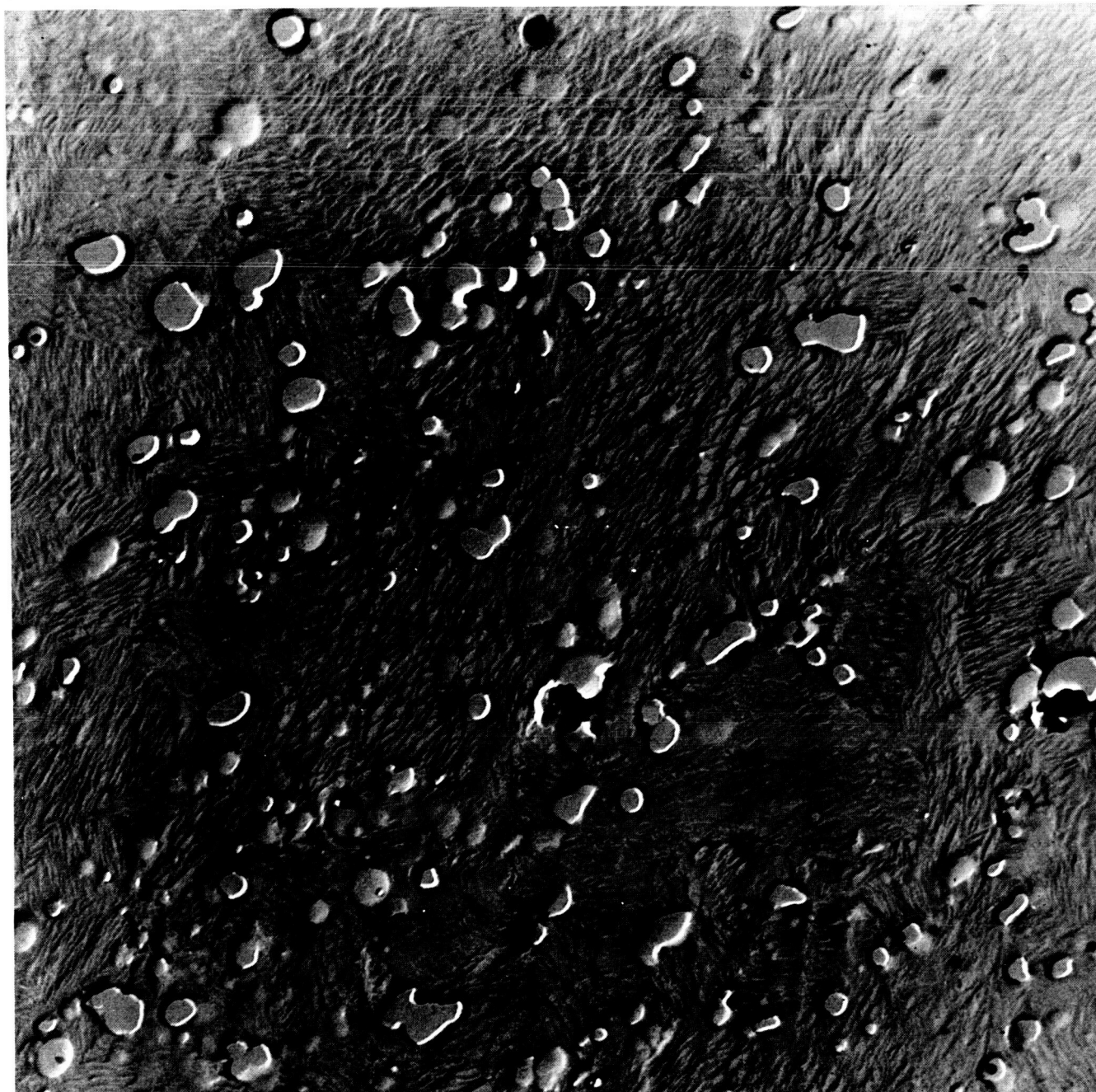


Figure 22: Electron micrograph of longitudinal section of alloy #6 (Ni-15% Mo + 7.5 V/o ThO₂) taken from the center of the extrusion. Etched, 20,000X

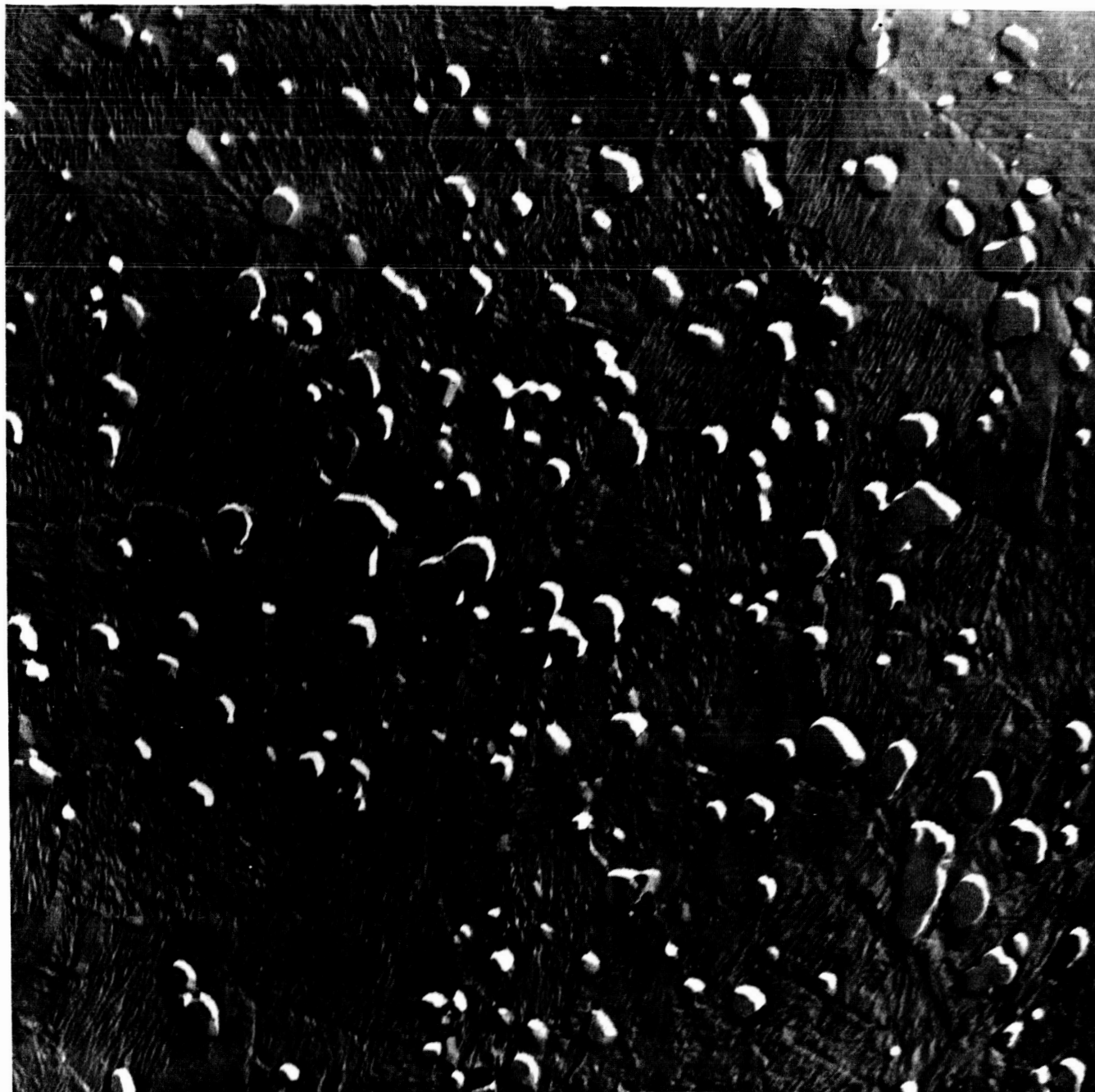
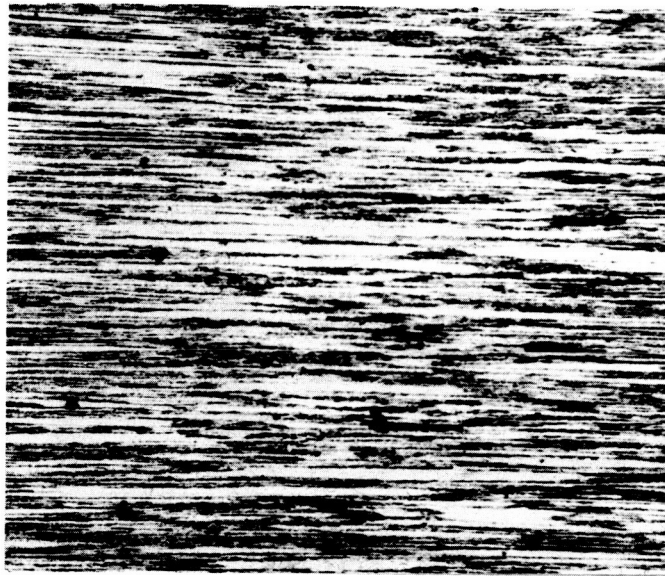
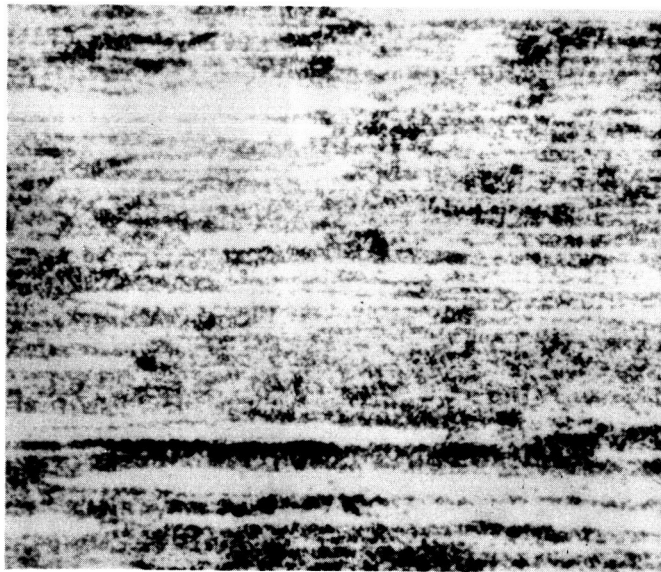


Figure 23: Electron micrograph of same section as Figure 22 after 100 hours at 2000° F
in vacuum (10^{-5} mm Hg). Etched, 20,000X



100X



1000X

Figure 24: Microstructure of longitudinal section of alloy #7 (Ni-15% Mo + 7.5
 $\text{V/o Al}_2\text{O}_3$) taken from the center of the extrusion.

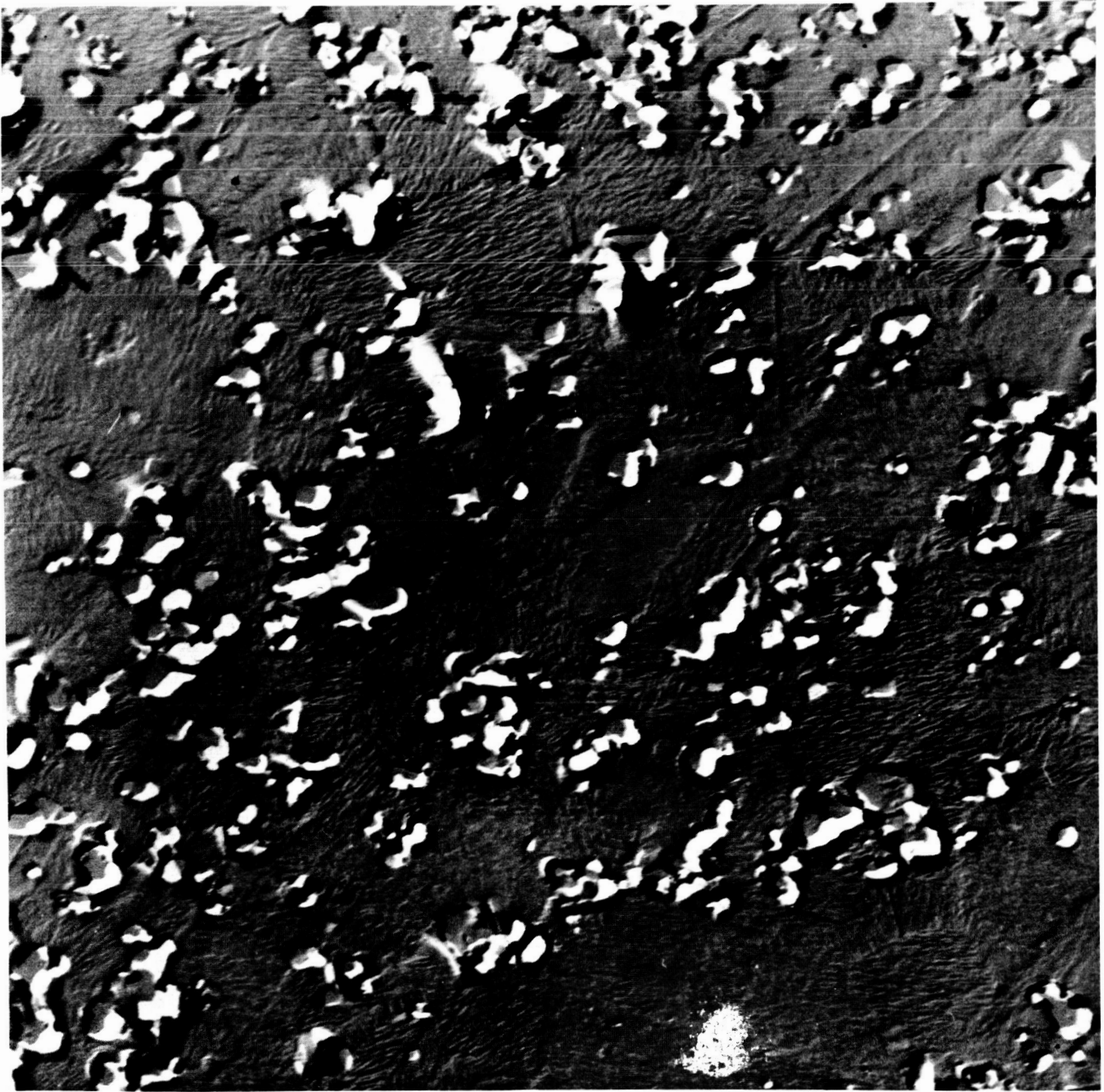


Figure 25: Electron micrograph of longitudinal section of alloy #7 (Ni-15% Mo + 7.5 % Al_2O_3) taken from the center of the extrusion. Etched, 20,000X

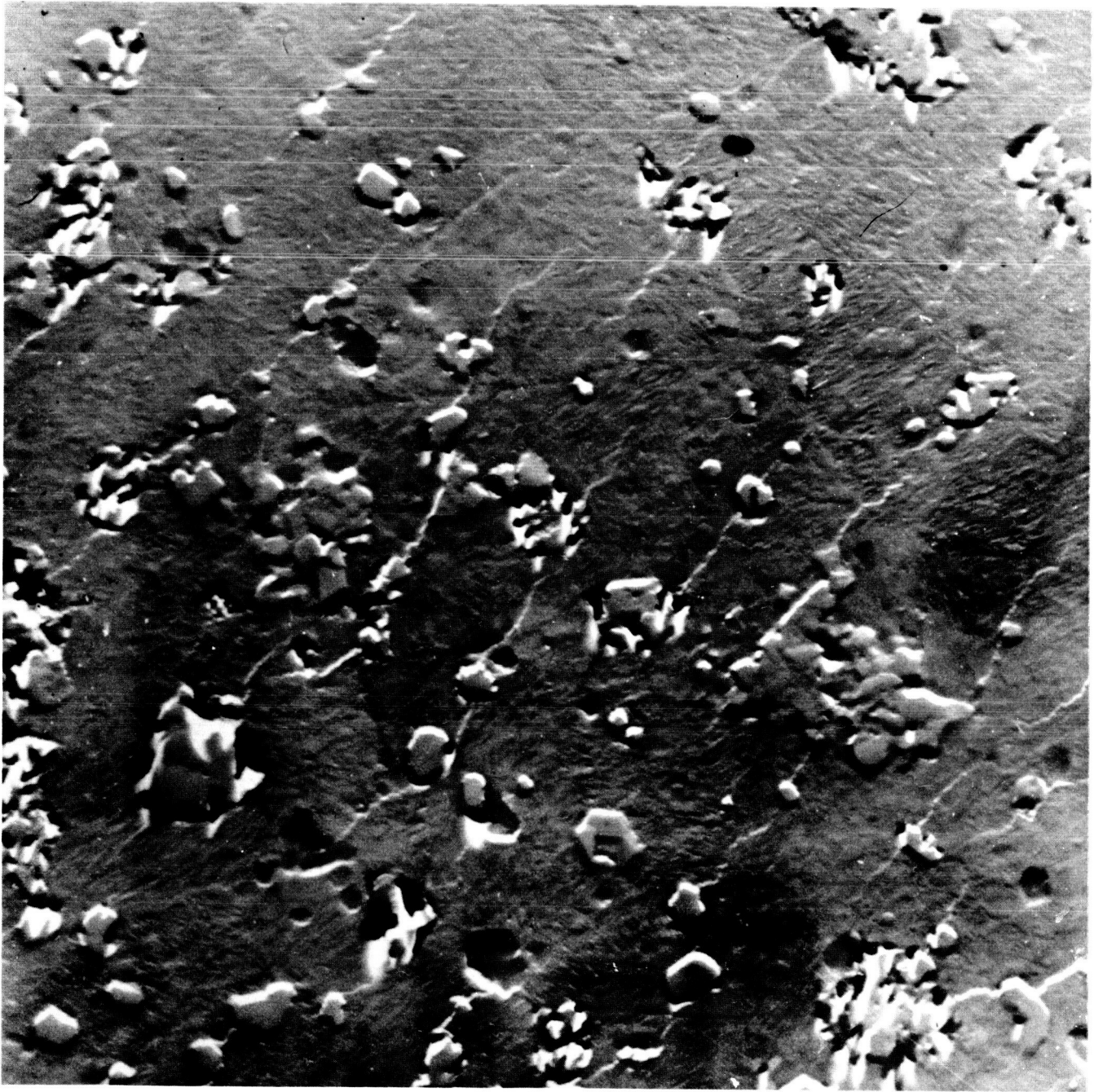
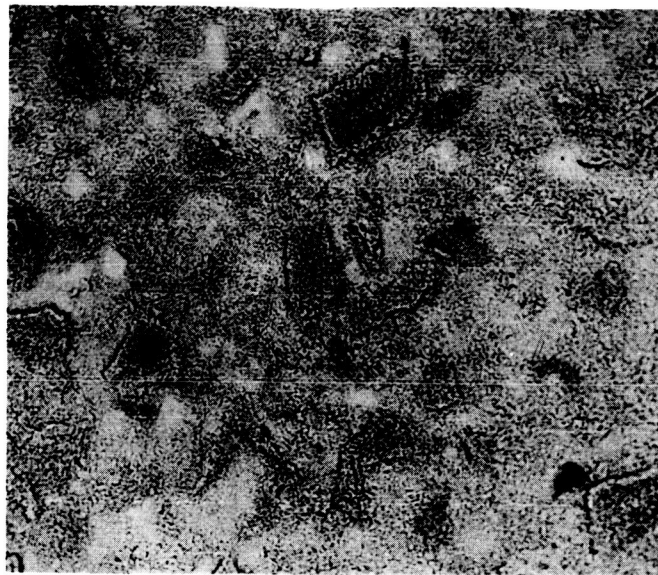
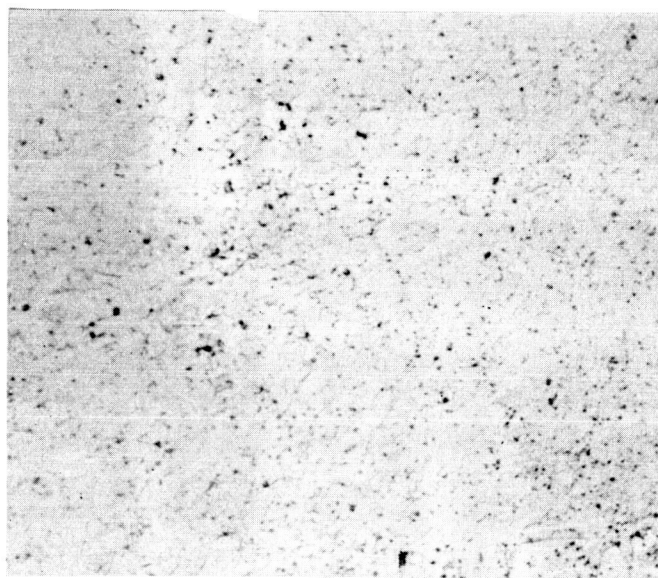


Figure 26: Electron micrograph of same section as Figure 25 after 100 hours at 2000° F
in vacuum (10^{-5} mm Hg). Etched, 20,000X

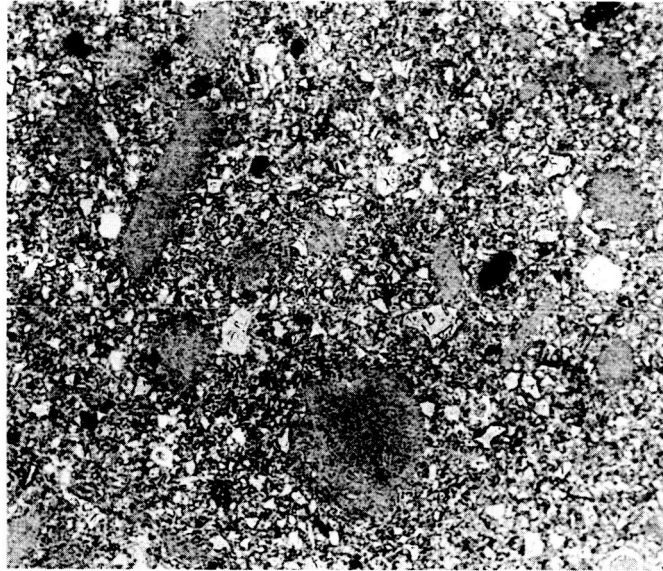


100X

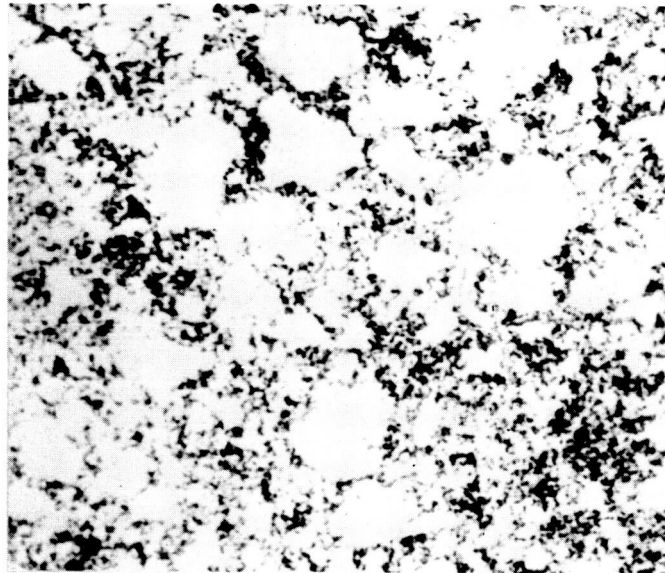


1000X

Figure 27: Microstructure of transverse section of alloy #2 (Ni-15% Mo + 2^v/o ThO₂) taken from the center of the extrusion.

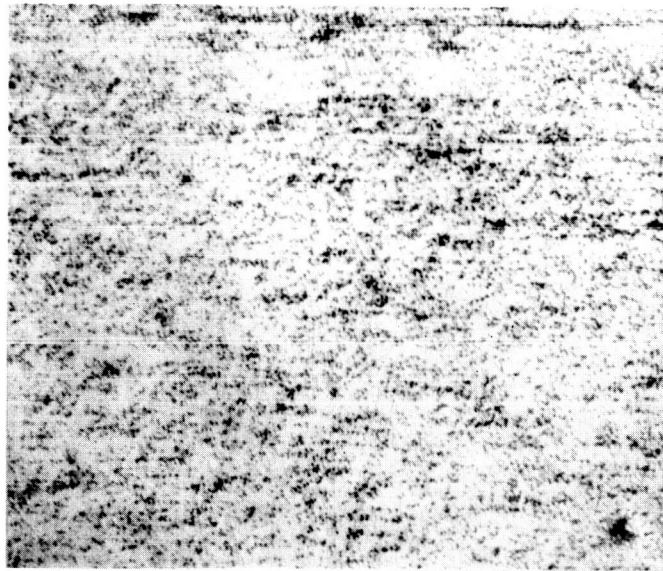


100X

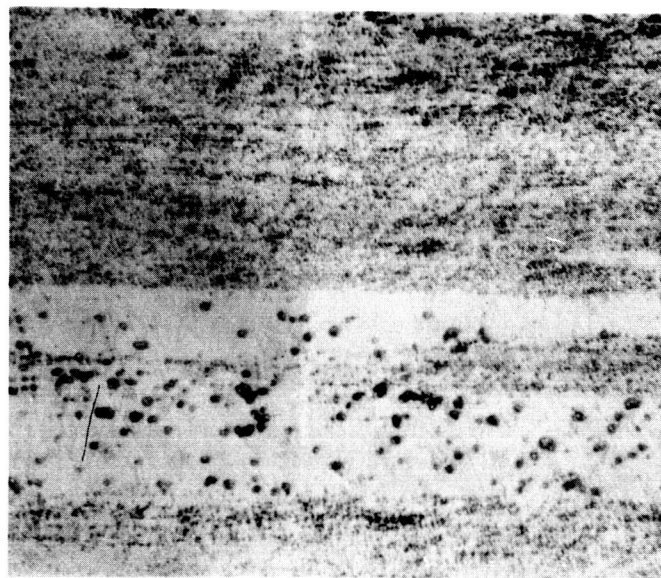


1000X

Figure 28: Microstructure of transverse section of alloy #7 (Ni-15% Mo + 7.5 ^v/o Al₂O₃) taken from the center of the extrusion.



Typical Microstructure

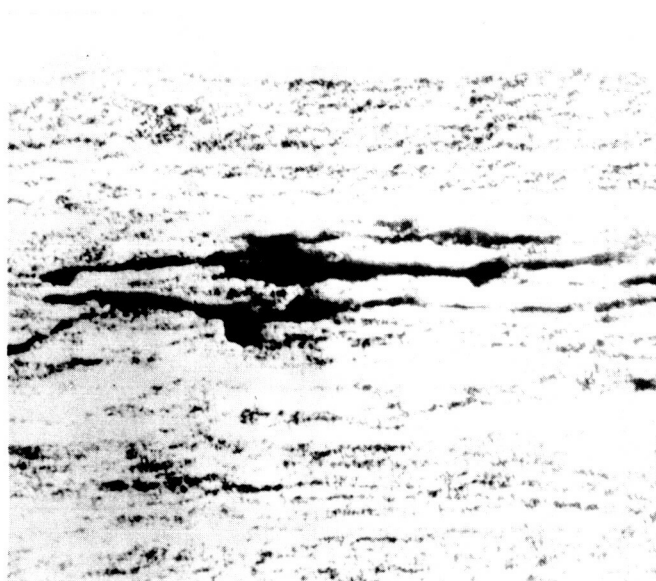


Local area with void formation

Figure 29: Microstructure of longitudinal sections of alloy #6 (Ni-15% Mo + 7.5 V/o ThO₂) taken from the center of the extrusion after 100 hours at 2000° F in vacuum (10^{-5} mm Hg). 1000X



Typical Microstructure



Local area with void formation

Figure 30: Microstructure of longitudinal sections of alloy #5 (Ni-15% Mo + 5 V/o Al_2O_3) taken from the center of the extrusion after 100 hours at 2000° F in vacuum (10^{-5} mm Hg). 1000X

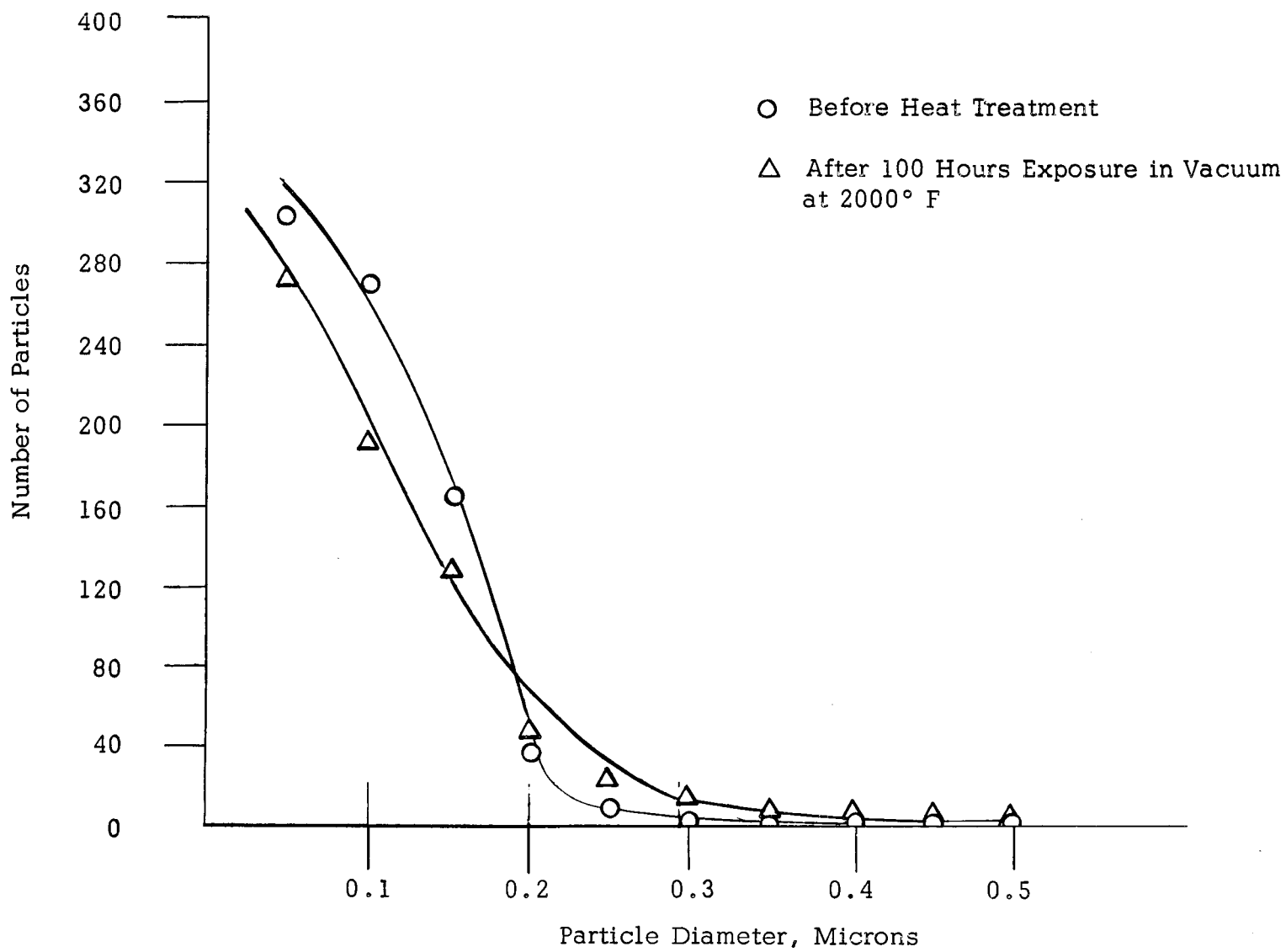


Figure 31: Particle Size Distribution for Alloy #2 (2 ^v/o thoria) Before and After Stability Test

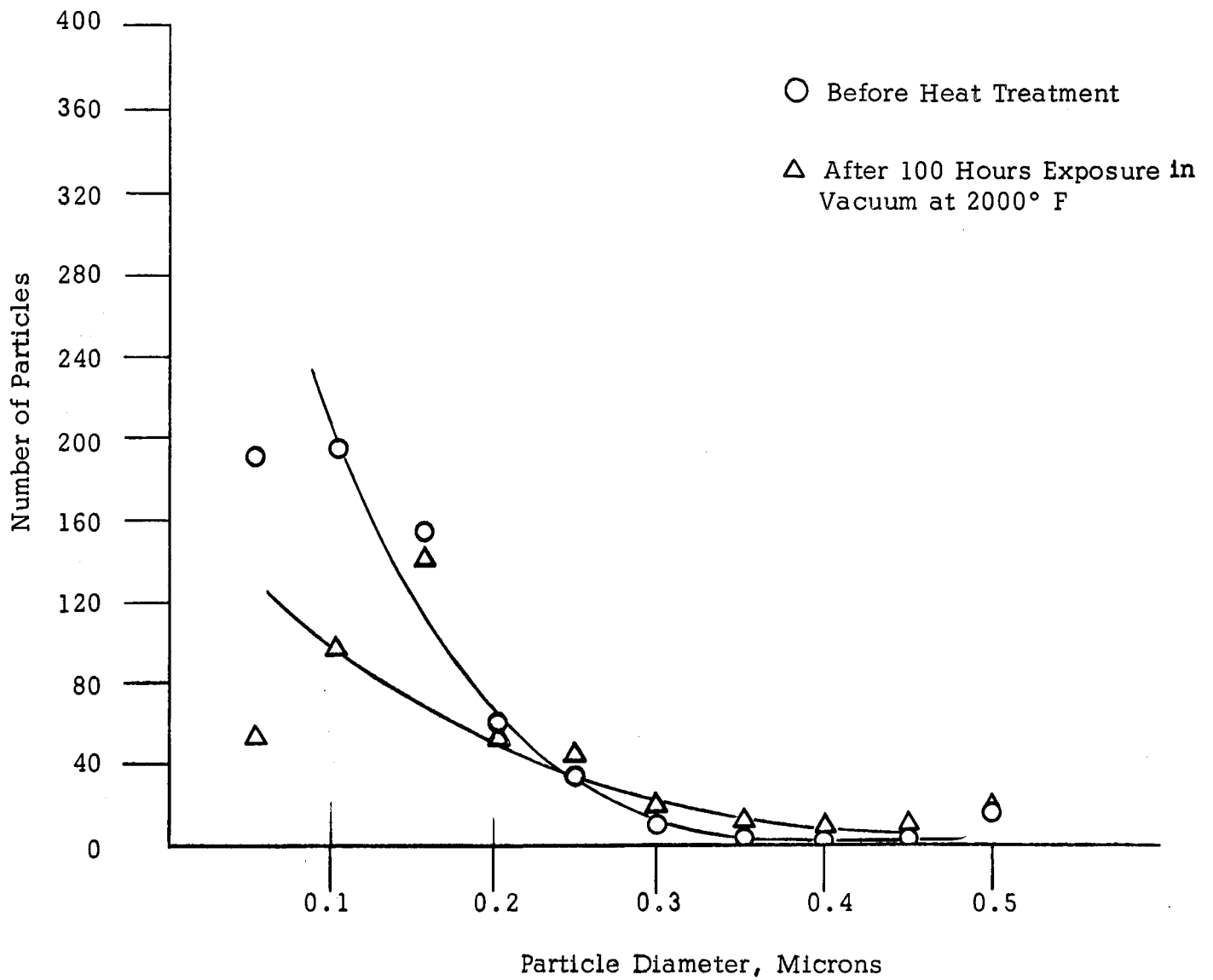


Figure 32: Particle Size Distribution for Alloy #3 (2 v/o alumina) Before and After Stability Test

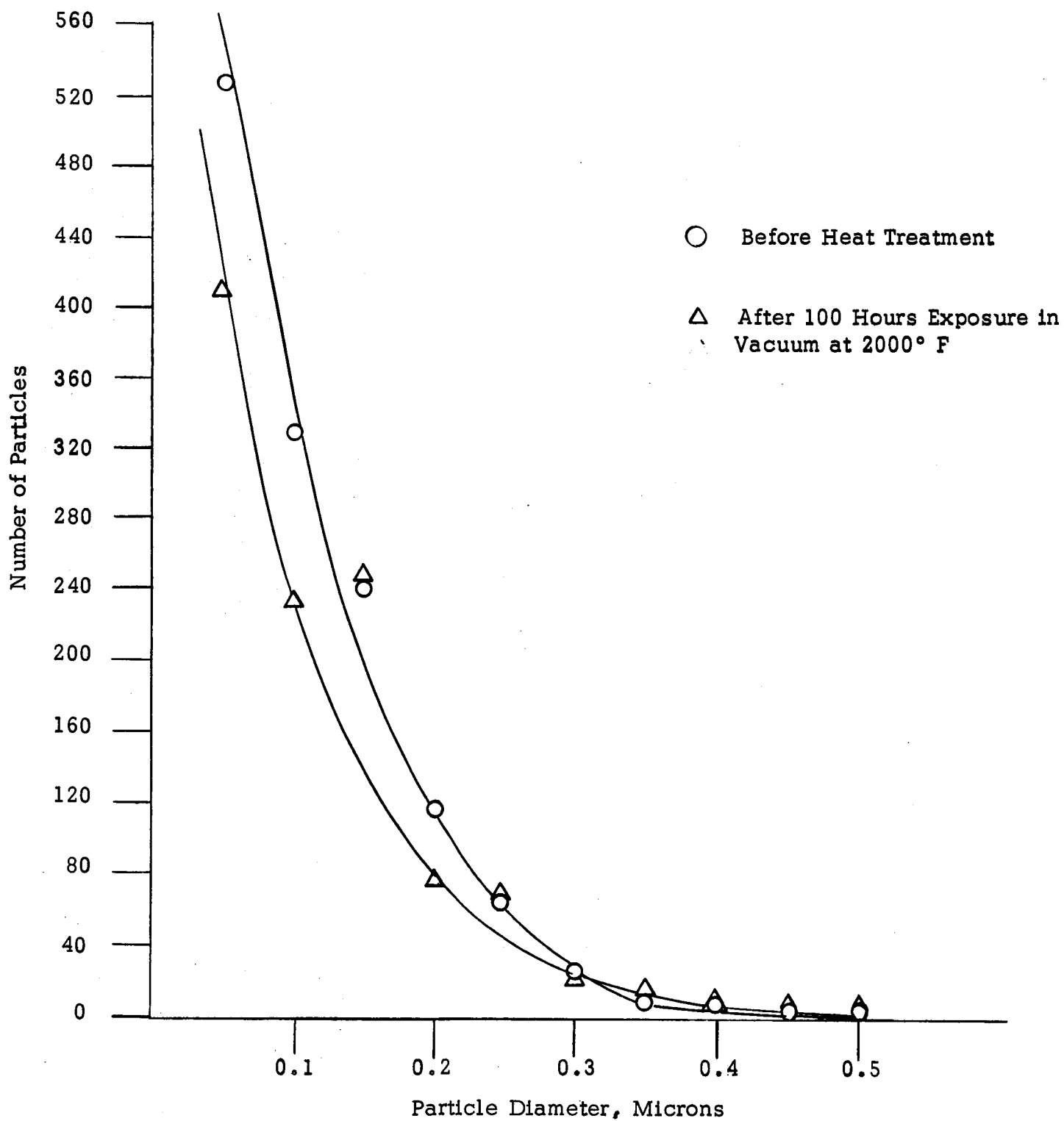


Figure 33: Particle Size Distribution for Alloy #4 (5 v/o thoria) Before and After Stability Test

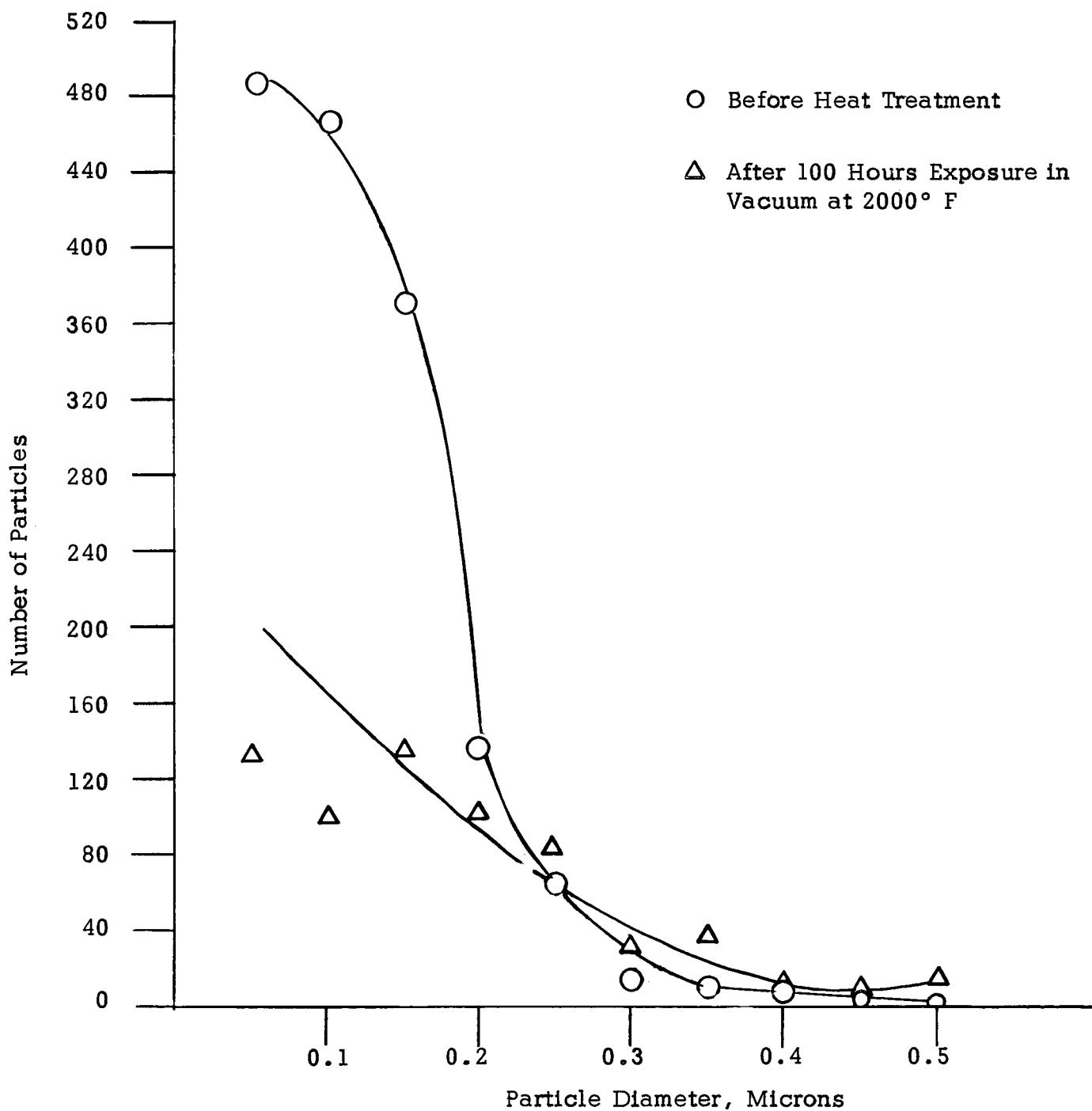


Figure 34: Particle Size Distribution for Alloy #5 (5 % alumina) Before and After Stability Test

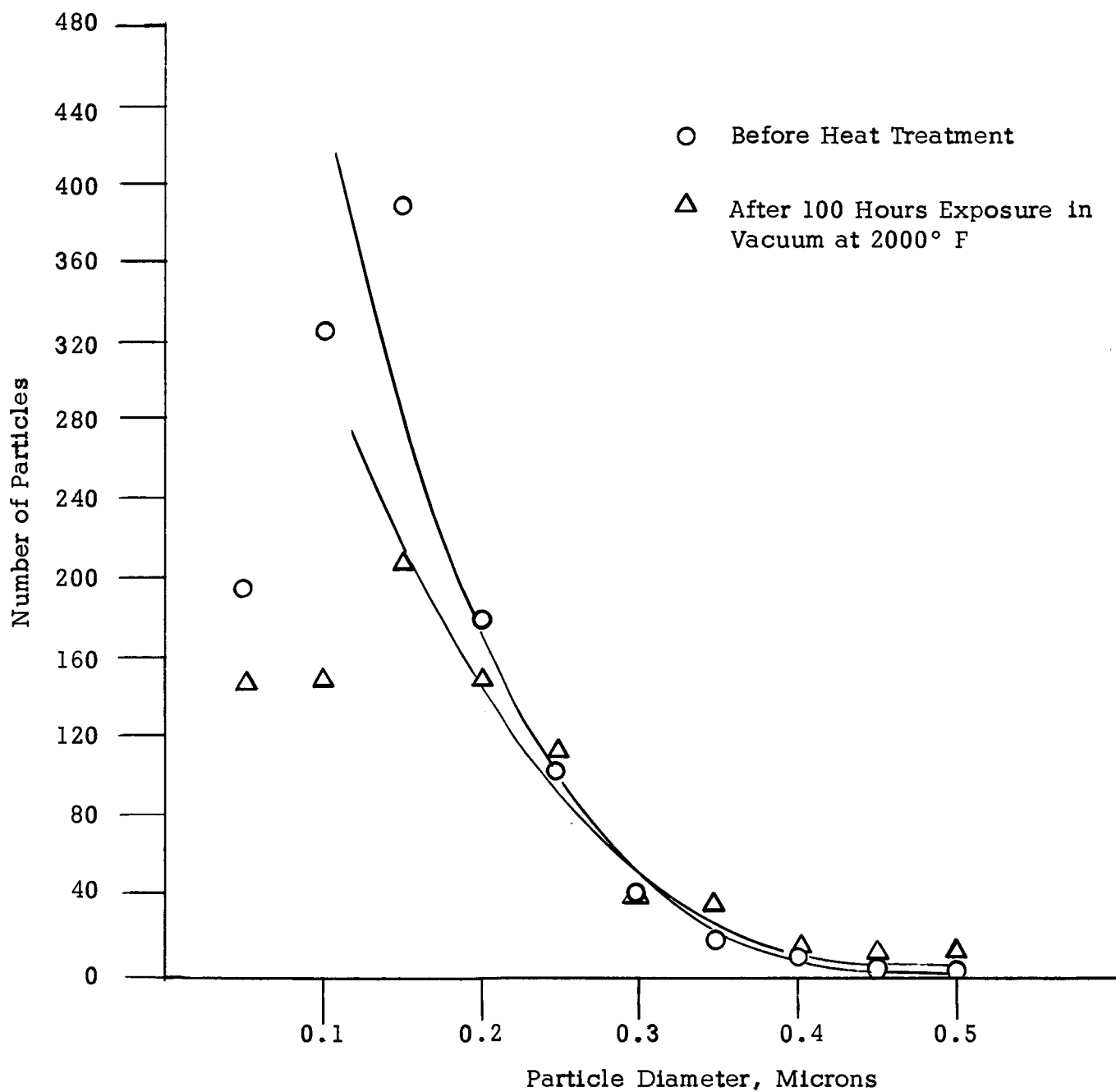


Figure 35: Particle Size Distribution for Alloy #6 (7.5 % thoria) Before and After Stability Test

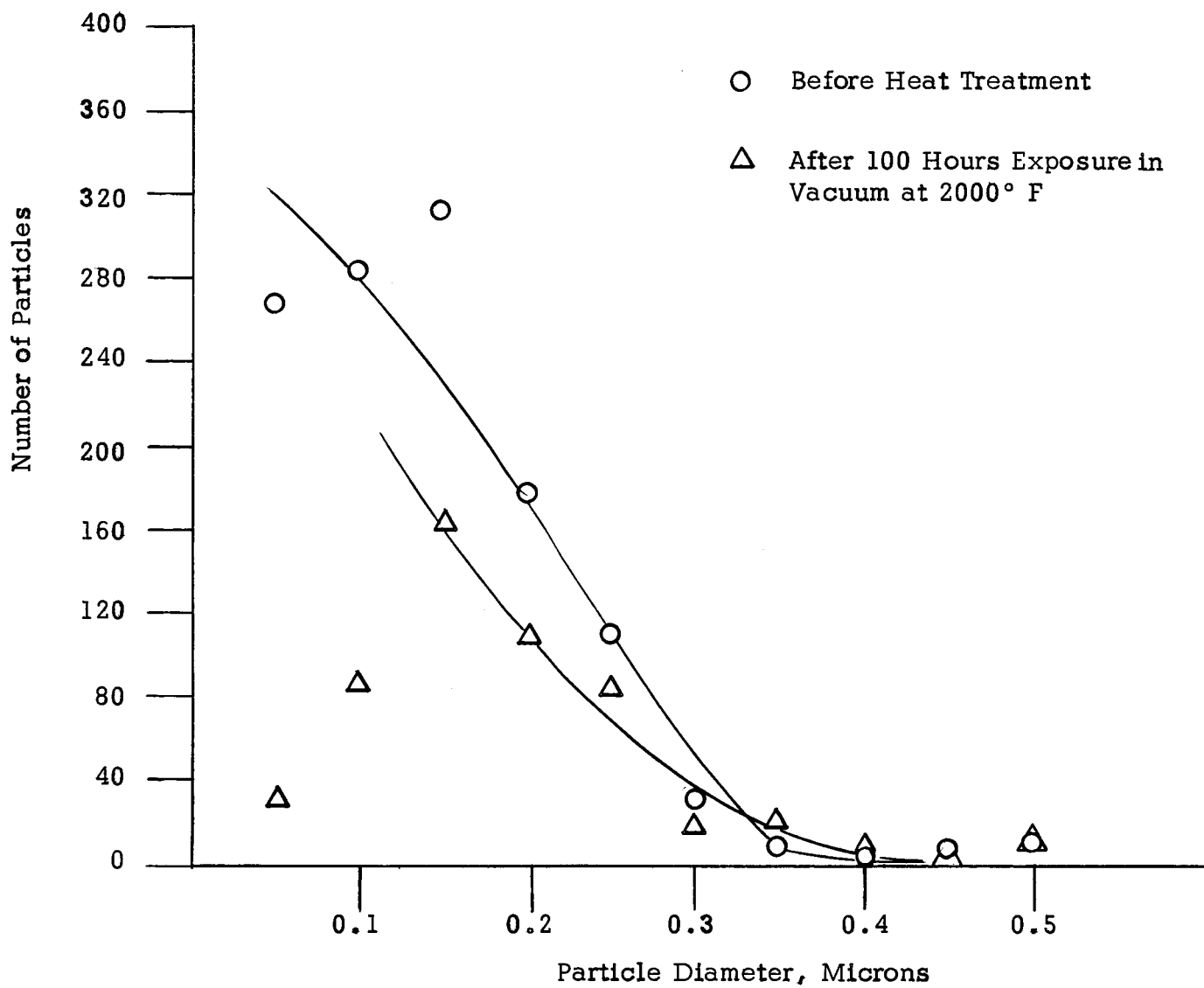


Figure 36: Particle Size Distribution for Alloy #7 (7.5 V/o alumina) Before and After Stability Test

APPENDIX I

A sketch of the fluidization column is shown in Figure A. In Table I of the Appendix, the analytical results are recorded. The samples represent mixtures of nickel oxide and molybdenum dioxide (separately ground to 0.2 microns). The mixtures were subjected to various conditions of time, temperature and atmosphere. No dispersoid was added to these mixtures. Sintering occurred during the fluidization. Sealing problem also occurred. Further work with the column was abandoned because the undertaking was too extensive for the scope of the program.

TABLE I

Reduction Experiments in a Fluidization Column

<u>Sample</u> ^a	<u>Temperature, °F</u>	<u>Time, Hours</u>	<u>Oxygen, %</u>
A-1	1500	0.5	-
A-2	1500	1.0	-
A-3	1500	5.0	0.52
A-4	1500	5.0	0.91
B-1	1800	0.5	1.41
B-2	1800	1.0	0.41
B-3	1800	5.0	-

^a Argon was used in heating up to test temperature, and then hydrogen was used for the remainder of test, except for A-4 in which hydrogen was used exclusively.

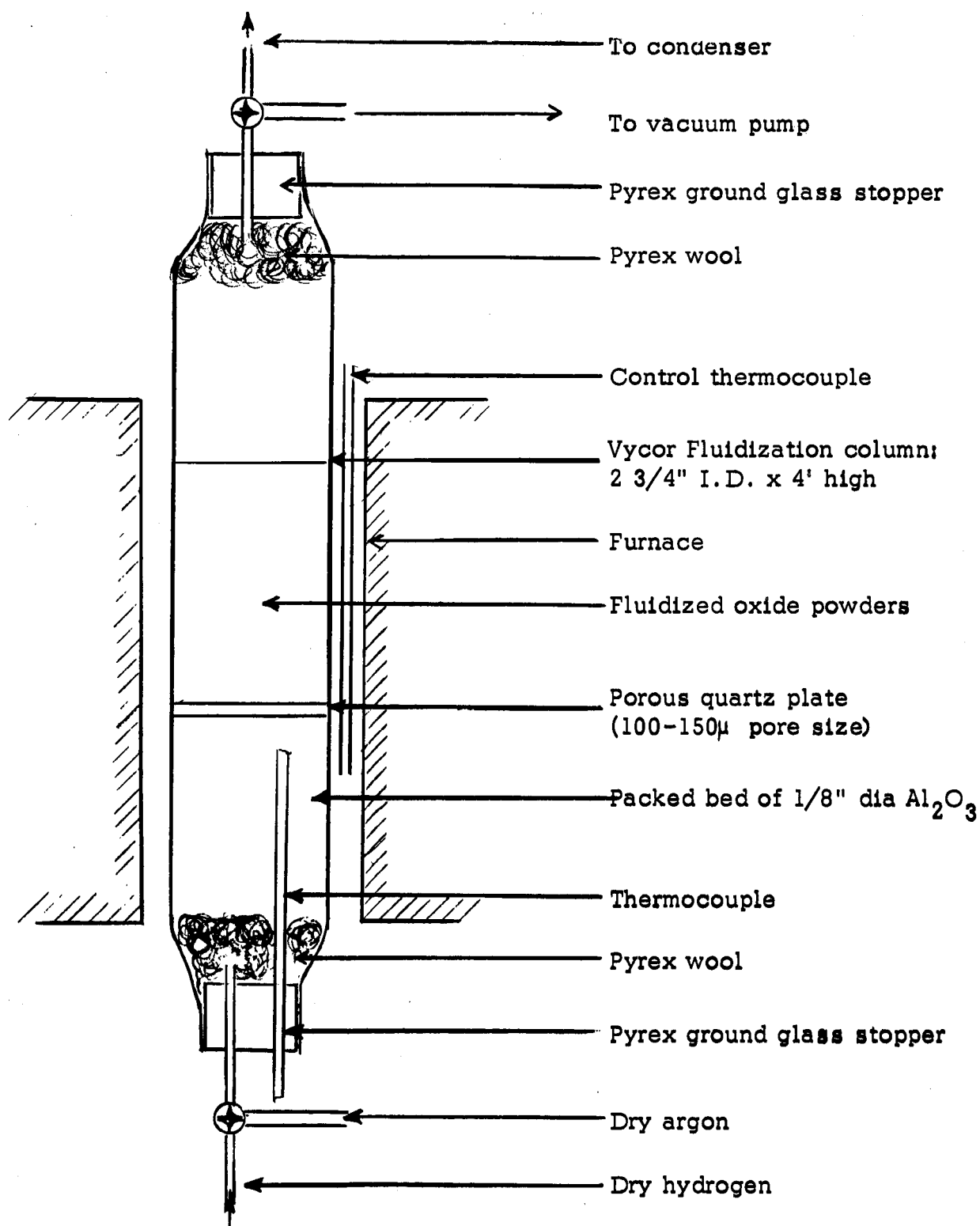


FIGURE A: Fluidization column for hydrogen reduction of NiO/MoO_2 powder.

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